CONFIDENTIAL

SUMMARY TECHNICAL REPORT

OF THE

NATIONAL DEFENSE RESEARCH COMMITTEE

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SUMMARY TECHNICAL REPORT OF DIVISION 8, NDRC

VOLUME 1

THE PREPARATION AND TESTING OF EXPLOSIVES

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT
VANNEVAR BUSH, DIRECTOR

NATIONAL DEFENSE RESEARCH COMMITTEE
JAMES B. CONANT, CHAIRMAN

DIVISION 8
RALPH A. CONNOR, CHIEF

WASHINGTON, D. C., 1946

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NOTES ON THE ORGANIZATION OF NDRC

The duties of the National Defense Research Committee were (1) to recommend to the Director of OSRD suitable projects and research programs on the instrumentalities of warfare, together with contract facilities for carrying out these projects and programs, and (2) to administer the technical and scientific work of the contracts. More specifically, NDRC functioned by initiating research projects on requests from the Army or the Navy, or on requests from an allied government transmitted through the Liaison Office of OSRD, or on its own considered initiative as a result of the experience of its members. Proposals prepared by the Division, Panel, or Committee for research contracts for performance of the work involved in such projects were first reviewed by NDRC, and if approved, recommended to the Director of OSRD. Upon approval of a proposal by the Director, a contract permitting maximum flexibility of scientific effort was arranged. The business aspects of the contract, including such matters as materials, clearances, vouchers, patents, priorities, legal matters, and administration of patent matters were handled by the Executive Secretary of OSRD.

Originally NDRC administered its work through five divisions, each headed by one of the NDRC members. These were:

Division A—Armor and Ordnance
Division B—Bombs, Fuels, Gases, & Chemical Problems
Division C—Communication and Transportation
Division D—Detection, Controls, and Instruments
Division E—Patents and Inventions

In a reorganization in the fall of 1942, twenty-three administrative divisions, panels, or committees were created, each with a chief selected on the basis of his outstanding work in the particular field. The NDRC members then became a reviewing and advisory group to the Director of OSRD. The final organization was as follows:

Division 1—Ballistic Research
Division 2—Effects of Impact and Explosion
Division 3—Rocket Ordnance
Division 4—Ordnance Accessories
Division 5—New Missiles
Division 6—Sub-Surface Warfare
Division 7—Fire Control
Division 8—Explosives
Division 9—Chemistry
Division 10—Absorbents and Aerosols
Division 11—Chemical Engineering
Division 12—Transportation
Division 13—Electrical Communication
Division 14—Radar
Division 15—Radio Coordination
Division 16—Optics and Camouflage
Division 17—Physics
Division 18—War Metallurgy
Division 19—Miscellaneous
Applied Mathematics Panel
Applied Psychology Panel
Committee on Propagation
Tropical Deterioration Administrative Committee

[redacted]

NDRC FOREWORD

As events of the years preceding 1940 revealed more and more clearly the seriousness of the world situation, many scientists in this country came to realize the need of organizing scientific research for service in a national emergency. Recommendations which they made to the White House were given careful and sympathetic attention, and as a result the National Defense Research Committee [NDRC] was formed by Executive Order of the President in the summer of 1940. The members of NDRC, appointed by the President, were instructed to supplement the work of the Army and the Navy in the development of the instrumentalities of war. A year later, upon the establishment of the Office of Scientific Research and Development [OSRD], NDRC became one of its units.

The Summary Technical Report of NDRC is a conscientious effort on the part of NDRC to summarize and evaluate its work and to present it in a useful and permanent form. It comprises some seventy volumes broken into groups corresponding to the NDRC Divisions, Panels, and Committees.

The Summary Technical Report of each Division, Panel, or Committee is an integral survey of the work of that group. The first volume of each group's report contains a summary of the report, stating the problems presented and the philosophy of attacking them, and summarizing the results of the research, development, and training activities undertaken. Some volumes may be "state of the art" treatises covering subjects to which various research groups have contributed information. Others may contain descriptions of devices developed in the laboratories. A master index of all these divisional, panel, and committee reports which together constitute the Summary Technical Report of NDRC is contained in a separate volume, which also includes the index of a microfilm record of pertinent technical laboratory reports and reference material.

Some of the NDRC-sponsored researches which had been declassified by the end of 1945 were of sufficient popular interest that it was found desirable to report them in the form of monographs, such as the series on radar by Division 14 and the monograph on sampling inspection by the Applied Mathematics Panel. Since the material treated in them is not duplicated in the Summary Technical Report of NDRC, the monographs are an important part of the story of these aspects of NDRC research.

In contrast to the information on radar, which is of widespread interest and much of which is released to the public, the research on subsurface warfare is largely classified and is of general interest to a more restricted group. As a consequence, the report of Division 6 is found almost entirely in its Summary Technical Report, which runs to over twenty volumes. The extent of the work of a division cannot therefore be judged solely by the number of volumes devoted to it in the Summary Technical Report of NDRC: account must be taken of the monographs and available reports published elsewhere.

In most of the projects undertaken by NDRC it was necessary to begin with a program of fundamental research in order to understand the problems to be solved. To Division 8 came many requests for fundamental research in problems concerning high explosives and propellants. The information obtained from these studies was useful in designing many new weapons and developing several new manufacturing processes, including an improved process for RDX and the development of molded composite rocket propellants and albanite, a propellant which eliminates flash from Navy guns. The fundamental information obtained from these studies, which has also been applied to programs outside NDRC efforts, will be of lasting usefulness and is perhaps the Division's greatest achievement.

To carry out the work, the Division, together with its contractors, employed the services of a group of highly skilled scientists, under the leadership of first G. B. Kistiakowsky and later Ralph A. Connor. This Summmary Technical Report, prepared under the direction of the Division Chief and authorized by him for publication, is a record of the Division's accomplishments and a tribute to the scientific integrity of the men who loyally served in it. They deserve the grateful appreciation of the Nation.

Vannevar Bush, Director
Office of Scientific Research and Development

J. B. Conant, Chairman
National Defense Research Committee

FOREWORD

The summary of the work carried out by Division 8 of the National Defense Research Committee [NDRC]—The Division of Explosives—is intended to give the reader an understanding of the scope of the Division's activities and to present briefly the results. Therefore, only limited experimental data are included: it is expected that those who wish more than a superficial knowledge of a particular field will refer to the original reports which are cited as references in the body of the summary. The work of Division 8 has been closely related to the work of Divisions 2 and 3 and it may be helpful to describe here the distribution of activities.

It was originally intended that Division 8 should include in its program the effects of explosives in liquid and gaseous media, while Division 2 should explore the effects in solids and in semi-solids, such as soils. While this assignment of responsibilities did guide the planning of programs it was not logical to follow it exactly; thus Division 8 undertook research on fragmentation, cavity charges, and certain phases of the work on air blast. In June 1944, the program on underwater explosives and explosions and the Division 8 work on air blast was transferred to Division 2; the summary report of Division 2 will therefore be of interest to those interested in high explosives since it contains both Division 2 and Division 8 information on air blast, underwater explosions, and terminal ballistics.

In the NDRC program on rockets, Division 3 carried out the design of rocket weapons and most of the work on conventional processes for solvent-extruded and dry-extruded double-base powders. This work is described in the summary report of Division 3. Division 8 carried out the research on new rocket powders, on new processes for conventional powders, and on stability determination and analytical methods for all propellants.

Division 8 did not attempt to set up and carry out a comprehensive program covering the entire field of explosives. The initial program was almost entirely of a fundamental and long-range character, with emphasis on synthetic research with some fundamental theoretical and experimental work on high explosives. As the fundamental research began to produce results, the high explosives program changed to the development of processes and the major emphasis in high explosives was directed toward the physical chemistry of explosives and, later, toward the application of this knowledge to the evaluation of weapons and the development of new weapons. The summary of the work on high explosives will therefore contain information on the following broad subjects: synthetic work, the development and application of methods for the evaluation and comparison of explosives and loaded munitions, the development of explosive compositions and devices, studies of the effects of explosions, and studies of the processes of detonation and its initiation.

After the program on high explosives was under way, Division 8 began its program on rocket propellants and, still later, on gun propellants. The summary of the work on propellants will therefore deal with the following: theory of the burning of propellants, molded composite propellant for rockets and jet propulsion units, solvent-extruded composite propellants for rockets, cast propellants for jet propulsion devices, gun propellants, and methods for the analysis and testing of propellants.

The last general field to be studied by Division 8 concerned tracers and igniters; the major objective was improved stability. Later, the development of a dim igniter was undertaken.

The evolution of the Division 8 program was the result of problems which originated within the Services or which were suggested by the Division and then sponsored by the Services. Those programs which resulted in practical developments were the result of good cooperation, and it is a pleasure to express the Division's appreciation to those within the Bureau of Ordnance, Army Air Forces, and Ordnance Department who contributed to this work.

This summary has been constructed from a large number of reports on individual problems and has been written by persons having first-hand familiarity with the projects about which they have written. Many of these authors have delayed their return to their permanent positions or have contributed their free time to the preparation of their summaries. Acknowledgment is made here to these persons as a group; they are named individually at the beginning of each section of the summary. The value of the summary is due directly to their cooperation in preparing this material and to the efforts of Dr. A. H. Blatt who planned the summary, guided the preparation of the various sections, and edited the final draft for submission to the Summary Reports Group.

Ralph A. Connor
Chief, Division 8

CONTENTS

INTRODUCTION

This section of the Summary Technical Report will attempt to summarize the specific adoptions and developments of Division 8 which will be of general interest. It should be emphasized, however, that the greatest contributions of the Division will probably not be enumerated in listing the specific accomplishments. In practically every problem that was presented it was necessary to carry out fundamental research in order to understand the problems to be solved. The fundamental information so obtained and the advice of the Division 8 personnel experienced in these fields has been felt in the design of many weapons and in the developments of many programs which cannot be attributed directly to NDRC. This fundamental information will be of lasting usefulness and perhaps represents the greatest achievement of Division 8.

A new and improved process for the manufacture of RDX was developed by the Division and was utilized for the production of about 360 tons of RDX per day. In addition to developing the process, additional problems were solved, including the incorporation of RDX with TNT in the preparation of Composition B, a process for the recovery of waste acid from the mother liquor, and the development of a substitute for beeswax in order that Composition A might be available on the scale necessary. This also led to an extensive research program on Torpex, and ultimately methods were developed for desensitizing this material and for the prevention of gassing during the storage of Torpex loaded munitions.

A process was developed for the preparation of the intermediates for Haleite, and improvements were made in the nitration process. A plant to produce this explosive and its intermediates, based upon this work, was beginning production when the war ended. Stability studies were an important part of both the propellants and high explosives programs, and the results obtained in such investigations were directly responsible for changes in the 5″ AA shell which decreased the probability of explosion when these shells were held in hot guns, for a change in the refining procedure of PETN, for the improved stability of aluminized explosives, including Torpex which was mentioned above, and for the adoption of a binder for tracer compositions which was used in production and gave improved stability to tracer ammunition.

Molded composite rocket propellants were developed and were ultimately made in diameters up to 12 inches. Grains having a diameter of 8½ inches were successfully used for launching the JB-2 weapon, and a plant to manufacture these charges was about 90 per cent completed when the war ended.

In order to eliminate flash from Navy guns a new propellant, Albanite, was developed, adopted by the Navy, and plans to produce this material were being made when the war ended. This propellant required the use of an explosive material, DINA, which had not been prepared prior to the war, and a process for manufacturing this was developed by Division 8.

One of the solvent extruded composite propellants developed by Division 8 was produced for use in the bazooka for the elimination of particle blast. It was known as BBP (Blastless bazooka powder).

Among the incompleted projects of the Division which may ultimately result in important weapons, the following subjects of investigation may be mentioned:

1. Shaped Charge Bombs
2. Antisubmarine Shaped Charge Bombs
3. The Shaped Charge Follow-Through Rocket
4. Shaped Charge Warheads for Naval Torpedoes
5. Antisubmarine Shaped Charge Follow-Through Bombs
6. Liquid Explosives
7. RDX Gun Powders
8. Powder and Head for the Super Bazooka
9. Powder for the Super 4.5″ Rocket
10. Improved Plastic Explosives
11. A process for the Preparation of Picric Acid from Benzene in One Step
12. The Explosive and Liner for a Spherical Grenade (BEANO)

The detailed descriptions of these and other projects are to be found in the seven chapters of the Summary Technical Report which follow.

Chapter 1

PREPARATION OF HIGH EXPLOSIVES

As part of its work on high explosives, Division 8 of the National Defense Research Committee [NDRC] undertook to prepare a number of candidate materials in sufficient quantity to permit an evaluation of their explosive properties. Some of the candidate explosives were chosen because they had been suggested in the open or classified literature; others were chosen because they, or the intermediates leading to them, had become available as a result of developments in the organic chemical industry in the past twenty-five years. This program naturally resulted in the preparation of a large number and variety of compounds.

For those candidate explosives whose properties merited the effort, attempts were made to develop commercially applicable methods of synthesis. When these attempts were successful and the explosive seemed likely of adoption, the syntheses were put through the pilot plant stage. When a development reached this point it was usually desirable to make a rather detailed study of the mechanism of the reactions involved in order to determine what by-products were formed. In addition studies of the preparation and properties of analogs of the successful candidate explosive were called for. The most important developments were the combination process for preparing RDX, the synthesis of Haleite, the synthesis of DINA, and the oxynitration of benzene to yield picric acid. These and the less spectacular results of the program are described in Sections 1.1[a] through 1.9 below.

The work described in the last paragraph dealt with pure compounds. Much additional work was devoted to explosive mixtures, for World War II saw the utilization in quantity of plastic explosives, of explosive compositions in which a powerful but sensitive explosive like RDX is desensitized by admixture with wax and/or a less sensitive explosive like TNT, and of aluminized compositions. Work with these three groups of explosives is detailed in Sections 1.10 through 1.12.

[a] This section is based on a summary prepared by Marvin Carmack.

1.1 THE PREPARATION OF RDX BY THE DIRECT NITROLYSIS OF HEXAMINE

One of the first explosives problems investigated by the NDRC was the preparation of RDX. Studies of the direct nitrolysis of hexamine were begun in the latter part of 1940. Somewhat later most of the effort was diverted to the alternative procedure, known now as the combination process. Work on the direct nitrolysis is summarized in the present section, and the development of the combination process and a comparison of the two processes are treated in Section 1.2 below.

In January 1941 a report[b] summarizing the work of the NDRC investigators carried the conclusion that there was then sufficient information available to permit the commercial production of RDX, but that much additional work was necessary in order to bring the cost of the material down to a reasonable figure.[1]

In the report just mentioned the most detailed NDRC information came from the investigators working at the Pennsylvania State College. This group studied both batch and continuous nitrolysis of hexamine. The most favorable results in batch runs were obtained with a ratio of 10 parts of nitric acid of at least 92% concentration to one part of hexamine, the reaction being carried out during 25 minutes at 25 to 30 C; the yield was 65 to 70%. The presence of sulfuric acid was found to be deleterious, and the addition of any of a number of salts either had no effect or decreased the yields of cyclonite.

For the continuous preparation of cyclonite by nitrolysis a small glass unit was developed. This unit had an output of 2.5 kg of cyclonite per day. The proportions of materials and yields were essentially the same in the batch and the continuous processes, the chief difference in the methods being the manner of mixing the hexamine and nitric acid. The reaction

[b] This report contains not only the results of the NDRC investigations but also data from Picatinny Arsenal, the Hercules Powder Co., E. I. du Pont de Nemours and Co., and from the Canadian investigators working on Project CE-12 at the University of Toronto.

chamber consisted of a glass tube 16 mm in diameter into which the strong nitric acid at between —10 and —5 C could be led and mixed with solid hexamine introduced by means of a mechanically operated aluminum screw device. Dissipation of the heat of reaction was the most difficult problem of the continuous process.

The final report of the Pennsylvania State College group gave detailed information on the development of a continuous process for the nitrolysis of hexamine.[2]

The results were based partly upon batch runs under varied conditions, and partly upon results obtained in three different models of apparatus for continuous nitrolysis.

In batch runs the best yield was obtained by the addition of 10 g of hexamine to 100 parts of 99% nitric acid (N_2O_4-free) at temperatures not exceeding 0 C during a period of 30 minutes. After the reaction mixture had stood for an additional 45 minutes, it was drowned in 500 ml of water and furnished a 90% yield of cyclonite. When the nitrolysis was carried out at 8 to 10 C during one hour, with an additional one-hour holding period, a yield of 84.8% was obtained.

The cyclonite obtained by drowning the reaction mixture in water and filtering was finely divided and contained impurities which made it difficult to dry the product completely. Moreover, the filtrates obtained were unstable and liable to undergo spontaneous fume-off. Purification of the product by recrystallization from 70% nitric acid, or acetone, or 1-nitropropane was recommended.

A much more satisfactory method for the isolation of the cyclonite involved the initiation of a controlled fume-off to destroy formaldehyde and other by-products by oxidation to carbon dioxide with the formation of recoverable nitrogen oxides. The fume-off could be induced by pouring the reaction mixture, after a suitable period of holding to complete the nitrolysis, into sufficient hot water at 85 to 90 C to result in a final nitric acid strength not exceeding 70%. As soon as the vigorous and exothermic fume-off was proceeding smoothly with the evolution of quantities of nitrogen tetroxide, the temperature could be reduced to 75 C until the reaction was complete. Nitrogen oxides were collected in a cold trap. The acid remaining in the fume-off vessel consisted of 30 to 50% nitric acid with a layer of solid crystalline cyclonite. After the oxidative destruction of the by-products, the cyclonite was easily recovered in a state of high purity (mp 204 C) by filtering and washing. The product was nicely crystalline and easily dried, in contrast to material isolated by drowning. The fume-off method involved very little loss of cyclonite unless the nitric acid strength after dilution exceeded 70% concentration, above which some decomposition of the cyclonite occurred. The solid product isolated following fume-off contained only about 0.08% of occluded acidity, which could be decreased by prolonged boiling in water or by recrystallization from an organic solvent.

The simplest apparatus for continuous nitrolysis of hexamine consisted of a spherical glass reactor of 100-ml volume designed to operate at a reaction volume of 50 ml. It was provided with four openings in the top: an inlet for 98% white nitric acid from a precooling unit, a thermometer, an air-driven stirrer, and a mechanically driven aluminum screw feed for the introduction of powdered hexamine. A fifth opening in the bottom of the reactor was sealed to an inverted U tube which served to regulate the reaction volume and to permit the continuous withdrawal of reaction mixture into a holding vessel. The whole unit was immersed in a cooling bath. In a typical run, 98% white nitric acid and hexamine were introduced in the weight ratio of 14.2 to 1. During a run of 3¾ hours, a total weight of 1,360 g (79.7%) of cyclonite was produced from 1,080 g of hexamine. The temperature was held between —3 and 5 C during the nitrolysis.

The second apparatus for continuous nitrolysis was constructed from a block of aluminum into which a hole 2 in. in diameter had been drilled to serve as a reaction chamber. The reaction chamber was provided with stirrer, thermometer, an aluminum screw feed device for the introduction of hexamine, and entrance and exit openings for nitric acid and reaction mixture, respectively. The aluminum block was cooled during the reaction by circulating a stream of dry air, chilled to low temperature by liquid air, through the jacket surrounding the reactor. The nitric acid was precooled to between —10 and 0 C by passage through a coil chilled with cold air. In one run of three hours' duration, a total weight of 2,100 g of fumed-off cyclonite was prepared from 1,850 g of hexamine (72% yield). During the run the reaction temperature was maintained between —5 and 0 C; the mixture was held for fifteen minutes to complete the nitrolysis before the fume-off was initiated. Quantitative data on the cooling requirements were included in the report.

The third and largest continuous reactor consisted of a cylindrical, flat-bottomed aluminum pot reactor with a volume of three quarts, designed to operate with a reaction volume of one quart. It was provided

with a simple separatory funnel for the introduction of strong nitric acid, a funnel for the introduction of powdered hexamine, an air-driven stirrer, an overflow side-tube for removal of reaction mixture, and a coil of 39 ft of 0.25-in. OD aluminum tubing for cooling the reaction mixture. Pentane at a temperature between —80 and —60 C was pumped through the coil at such a rate that the reaction temperature was held at approximately 0 C. Detailed data on the cooling requirements were recorded to aid in the design of reaction units of plant scale. In a typical run at 0 C using an acid hexamine ratio of 16.4 by weight, a yield of 65.5% of dry, fumed-off cyclonite was isolated. The rate of production of cyclonite was of the order of 5 pounds per hour.

It was estimated that a 50-gallon Pfaudler unit should be able to produce at least 555 pounds of cyclonite per hour.

1.1.1 Important Variables in the Direct Nitrolysis Process

Nitric Acid Strength and Ratio of Nitric Acid to Hexamine

When a fixed weight ratio of 10 parts of nitric acid to one part of hexamine was used in a series of batch nitrolyses at 0 C, it was found that the yield of cyclonite was a nearly linear function of the strength of nitric acid between 88 and 99%, the yields varying from about 5 to 90% in that range. All runs were made with an addition time of 30 minutes, followed by a holding time of 30 minutes. In another series of experiments the strength of nitric acid was held constant at 98%, and the weight ratio of nitric acid to hexamine was varied. Above the ratio of 11/1 the yields of cyclonite remained approximately constant, but below that critical ratio yields fell off rapidly, reaching 64% at a ratio of 8 parts of 98% nitric acid to one part of hexamine.

Reaction Temperature

The yields were essentially constant at various temperatures up to about 5 C. Above 5 C the yields became progressively lower as the temperature increased; at 52 C only 53% of cyclonite was obtained with 10 parts of 98% nitric acid to one part of hexamine. It was recommended that the temperature of nitrolysis be maintained between 0 C and 5 C, not only to obtain the maximum yield of cyclonite, but also for maximum safety of operation. On the other hand it was pointed out that at a temperature of 8 to 10 C the yield is only slightly lower than 0 to 5 C, so that the economy effected by reduced refrigeration requirements at the higher temperatures might outweigh the slight loss in yield.

The heat of the nitrolysis reaction was found to be of the order of 500 calories per gram of hexamine. The removal of the heat of reaction and the prevention of local overheating where particles of solid hexamine come into contact with fresh nitric acid were found to be the most difficult factors to control in the nitrolysis reaction, particularly in the continuous reactors. The time of addition of hexamine in batch runs or the rate of feed of reactants in the continuous reactors, as well as the degree of agitation, have an important bearing on the control of the reaction temperature.

Purity of the Nitric Acid

The presence of nitrogen tetroxide in the nitric acid is undesirable, since the oxide seems to make the reaction mixture unstable and liable to fume-off. The higher the percentage of nitrogen oxides, the lower the temperature at which the fume-off is likely to occur. Another undesirable point suggested in connection with the presence of nitrogen tetroxide is that it probably results in the formation of traces of trinitrosotrimethylenetriamine; this material lowers the stability of the cyclonite. Nitric acid containing no more than 0.15% of nitrogen tetroxide apparently gave satisfactory results.

In an effort to find possible catalytic effects, a number of substances, mostly inorganic salts, were added to the nitrolysis mixture in a series of runs; in general the yields of cyclonite were either unaffected or were lowered. No desirable effects were observed with any of the added substances studied.

Time of Addition of Hexamine

It was suggested that this variable is related to the influence of temperature, since the decreases in yield resulting from too rapid addition of hexamine to the nitric acid are probably due to local overheating. The proper rate of addition will therefore be that which does not exceed the capacity of the apparatus to remove the heat of nitrolysis. The same statement applies to the rate of feed of the reactants in the continuous reactors.

Effect of Stirring

Vigorous stirring of the hexamine with the nitric acid is desirable to promote rapid solution of the solid

in the liquid and to avoid unfavorable local temperature and concentration effects.

Effect of Holding Time before Work-up of Nitrolysis Mixture

The reaction of hexamine was at first considered to be complete as soon as the hexamine had dissolved, but later investigations showed that holding the reaction mixture for an additional 15 to 20 minutes resulted in a gain of 5 to 10% in the yield of cyclonite. A holding period was made a part of the standard procedure.

Effects of Various Methods of Isolating Cyclonite

The controlled fume-off of the diluted reaction mixture was found to give a granular product of satisfactory purity and excellent crystalline properties. If the strength of nitric acid during the fume-off does not exceed 70% by weight, there is very little loss of cyclonite by decomposition. The procedure involving the drowning of the reaction mixture in cold water had the disadvantages that the solid cyclonite contained impurities which made it difficult to dry and handle, while the filtrates were unstable and tended spontaneously to undergo fume-off.

At about the time that the final report discussed in the preceding pages appeared, reports reached this country from England describing the continuous nitrolysis process developed there. The British process, known now as the Woolwich process, was in pilot plant operation, plans for acid recovery were well under way, and designs for a plant to produce 60 tons of RDX per week were in preparation. In view of this situation, and because of the promising results being obtained in the study of the synthesis of RDX using acetic anhydride (see Section 1.2), work on the nitrolysis of hexamine by NDRC investigators was suspended.

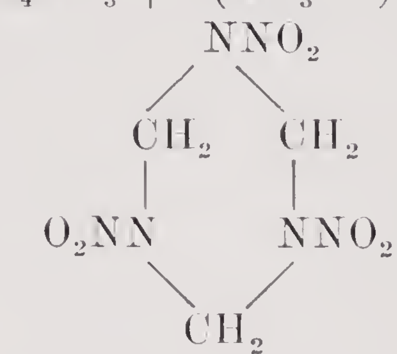
Much later, in April 1944, interest in the nitrolysis of hexamine was revived. As a preliminary to the setting up of a research program on this subject, a detailed review of the literature on the direct nitrolysis process was prepared.[3]

The changing military situation, however, and the need for the available investigators to work on another problem led in late June 1944 to the postponement of the experimental program, and in the fall of 1944 the decision was made not to undertake experimental work on the nitrolysis of hexamine.

1.2 THE COMBINATION PROCESS FOR THE PREPARATION OF RDX(B)[c]

Within a short time after research on RDX had been started, NDRC was advised that Canadian investigators had obtained a 40% yield of RDX by the interaction of approximately equivalent amounts of formaldehyde, ammonium nitrate, and acetic anhydride. The process may be represented ideally as follows:

$$3HCHO + 3NH_4NO_3 + 6(CH_3CO)_2O \rightarrow$$



$$+ 12CH_3CO_2H$$

This method avoids the destruction of formaldehyde and the enormous recovery of nitric acid characteristic of the nitrolysis reaction, but requires the use and recovery of a large amount of acetic anhydride.

At this time the United States had a large capacity for acetic anhydride, and the waste of formaldehyde and recovery of nitric acid in the direct nitrolysis of hexamine were considered more serious than the high consumption of acetic anhydride in the Canadian process. Consequently a study of the new Canadian method was begun. This was done first at the University of Michigan and later more extensively at Cornell University. The original Canadian method consisted of mixing all the reagents cold and warming until a vigorous reaction set in. It was shown very early at Michigan[4] that better yields were obtained by adding portionwise to a flask an intimate mixture of ammonium nitrate and paraformaldehyde, and a slight excess of acetic anhydride containing a trace of nitric acid. The reaction mixture is maintained at 75 C and stirred vigorously during the process. After the addition is completed the mixture is heated for a short period, diluted with warm water, chilled and the precipitated RDX removed by filtration.

At Cornell University[5,6] the Canadian process was subjected to a more thorough study, during which it was concluded that the best results were obtained by adding one mole of paraformaldehyde to a mixture of 1.25 moles of ammonium nitrate and 2.5 moles of acetic anhydride. After isolation in the usual way, the RDX was recrystallized from 55% nitric acid.

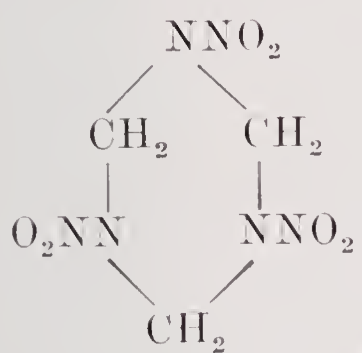
[c]This section is based on summaries prepared by S. R. Aspinall and Ralph Connor.

[redacted]

Studies were made of the optimum ratio of ingredients, the optimum temperature of reaction, the relative merits of different forms of formaldehyde, and the effect of free nitric acid and buffers. These studies, as well as a search for catalysts, failed to produce any significant improvement in the standard procedure, outlined above, which yielded about 55% of the theoretical amount of RDX calculated from formaldehyde. This process was used for a short time for full-scale manufacture in Canada, but active investigations of this method by NDRC ceased about December 1941 because of the promise of another process—the combination process which is described below.

As has been pointed out, the direct nitrolysis, ideally represented by reaction (1),

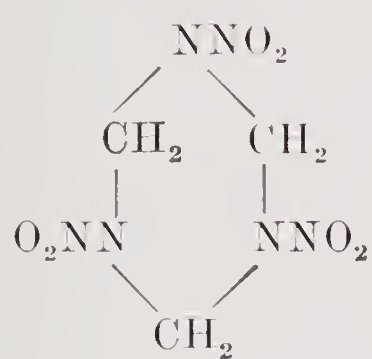
$(CH_2)_6N_4 + 4HNO_3 \rightarrow$



$+ 3HCHO + NH_4NO_3$ (1)

must be carried out with a large excess of nitric acid which results in the destruction of one-half of the formaldehyde introduced, and requires that an enormous nitric acid recovery system be made an integral part of the explosives plant. On the other hand the Canadian process, ideally represented by reaction (2)

$3HCHO + 3NH_4NO_3 + 6(CH_3CO)_2O \rightarrow$

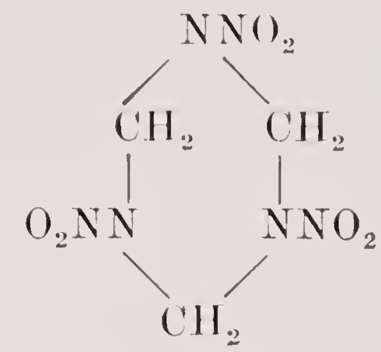


$+ 12CH_3CO_2H$ (2)

requires a large amount of acetic anhydride, half of which is consumed because formaldehyde and ammonia (as ammonium nitrate) are introduced into the reaction rather than hexamine (the dehydrated equivalent of formaldehyde and ammonia).

Since the two by-products of the nitrolysis reaction (1) are raw materials for the Canadian reaction (2), it is apparent that, if the nitrolysis reaction would occur under conditions favorable for the Canadian reaction, it would be possible to eliminate the disadvantages of both. By simple addition of reactions (1) and (2) one obtains reaction (3):

$(CH_2)_6N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2O \rightarrow$



$+ 12CH_3CO_2H$ (3)

In this reaction one makes use of the formaldehyde and ammonium nitrate formed in the nitrolysis and obtains *two* moles of RDX from each mole of hexamine and each 6 moles of acetic anhydride; furthermore, there is no nitric acid to be recovered. By the spring of 1941 this reaction, known as the combination process, had been run successfully at the University of Michigan, and by late 1941 it had shown such promise that all NDRC work on RDX after that time was directed toward its development. A great many modifications of the basic reaction were investigated at Michigan,[4,7] Cornell,[5,8] and Pennsylvania State College,[9] but the following may be considered typical.

Ammonium nitrate and acetic anhydride were placed in a flask and, while the mixture was stirred at 75 C, the following three liquids were introduced concurrently and proportionately: acetic anhydride, concentrated nitric acid, and a solution of hexamine in glacial acetic acid. The final mixture was held for a short time at 75 C, diluted with water to 30% acetic acid, and simmered to hydrolyze unstable reaction by-products, which are a mixture of various nitrated and acetylated derivatives of hexamine fragments. After simmering, the slurry is cooled and the precipitated RDX removed by filtration. The yield is 78% of the theoretical amount (2 moles) of RDX melting at 199 C. By dissolving the ammonium nitrate in the nitric acid, the process is made to consist of feeding three liquids (ammonium nitrate dissolved in nitric acid, hexamine dissolved in acetic acid, and acetic anhydride) into the reaction flask. This in effect put the reaction on a continuous basis and later a reactor was designed which was more suitable for continuous operations. This reactor consisted of a U-shaped tube with an arm connecting the upper ends of the U. During operation, the U tube is filled with reaction mixture which is circulated rapidly by a pump (propeller), and the three liquids are fed into one arm of the tube at the same rate that the reaction mixture overflows from the other. The effluent reaction mixture is held until a suitable volume has accumulated; it is then diluted, simmered, cooled, and the crude RDX removed by filtration.

The crude product from the combination process contains traces of acetic acid even after thorough washing, so it is desirable to recrystallize the product to reduce the acidity essentially to zero. A much more important reason for recrystallization is connected with the nature of the explosive product itself. All material produced by the combination process (as well as the Canadian process) consists of a mixture of RDX and HMX, the latter being present in amounts varying from 3 to 8% of the total when the process is carried out under optimum conditions. This mixture of RDX and HMX is hereafter designated as RDX(B). HMX is cyclotetramethylenetetranitramine (the eight-membered ring analog of RDX) and may arise from the eight-membered ring present in hexamine.

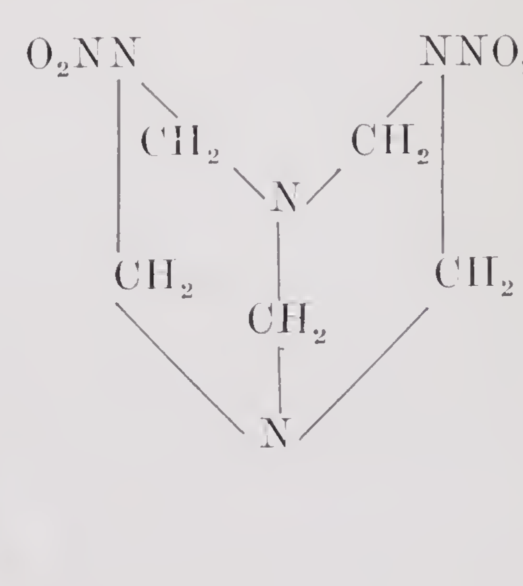
HMX is equivalent to RDX in power and is superior to RDX in chemical stability. HMX exists in four polymorphic modifications,[10-12] the stable one (β) of which shows about the same sensitivity to impact as RDX; however, the unstable polymorphic modifications of HMX are very sensitive, especially in certain crystal modifications.[13,14] Therefore, although the presence of HMX in the product from the combination reaction is not deleterious per se, it is essential for safety in manufacture and handling that the HMX be present only as the β-polymorph. The best method of insuring the exclusion of the unstable sensitive polymorphs is to recrystallize the product under equilibrium conditions. This can be done from any one of a great many solvents provided precipitation is done slowly and with adequate agitation. A convenient and economical way of conducting the crystallization is to dissolve the crude RDX in hot acetone and then blown in steam until the acetone is completely removed, leaving a slurry of RDX in water. The aqueous acetone which distils is suitable for immediate recovery; the acid-free mixture of RDX-β HMX is removed by filtration. This material is the end product of the preparative procedure and is ready for incorporation with other materials such as TNT, wax, or oil (Section 1.11).

1.2.1 The Mechanism of the Reaction

In connection with the development of the combination process an attempt was made to determine the exact chemical mechanism by which RDX is formed.[15-18] This study was undertaken primarily because of the feeling that ways to improve the yields beyond those which were obtained by an empirical approach would be arrived at only if the true nature of the reaction was understood. This work was conducted by allowing hexamine to react with each and all of the other ingredients of the combination process, in various ratios and under various conditions. By this means it is possible to prepare a large number of compounds, some of which are actually formed as by-products in the combination process and some of which are never isolated under conditions prevailing in the process. For example, by treating hexamine with acetyl nitrate (an equimolecular mixture of acetic anhydride and nitric acid $Ac_2O + HNO_3 \leftrightarrows AcONO_2 + AcOH$) one obtains a series of four compounds which represent different degrees of attack of the hexamine molecule by the reagent. If 1 mole of acetyl nitrate is used, the product is a derivative of an unbroken hexamine molecule; 2 moles of acetyl nitrate produce a cyclic pentamethylenetetramine derivative in which one carbon atom is lost but the basic ring structure of hexamine is preserved; 3 moles of acetyl nitrate produce a derivative of linear pentamethylenetetramine in which one carbon atom of the original hexamine is lost and the ring structure is destroyed; 4 moles of acetyl nitrate produce a derivative of linear tetramethylenetriamine in which an additional carbon atom and a nitrogen have been lost.

The product from 1 mole of hexamine and 4 moles of acetyl nitrate, which has the structure CH_3CO_2-$CH_2N(NO_2)CH_2N(NO_2)\ CH_2N(NO_2)\ CH_2O_2CCH_3$ and is designated BSX, is apparently the end product of the interaction of the two materials and actually appears as a by-product of the combination reaction; it is one of the unstable compounds hydrolyzed in the simmering process. Although BSX is the only one of the acetyl-nitro derivatives of the linear polymethyleneamines positively demonstrated to be present in crude RDX(B), it is quite likely that other related compounds are likewise present and are destroyed by simmering. By conducting the combination process in the cold, BSX is the major product of the reaction.[7]

If the product obtained from hexamine and 2 moles of acetyl nitrate, which has the structure



and is designated DPT, is isolated and then treated with 1 or 2 moles of acetyl nitrate, one obtains two compounds which are not the same as those obtained from hexamine and 3 or 4 moles of acetyl nitrate respectively, indicating that DPT and the products from hexamine and 3 or 4 moles of acetyl nitrate have a common precursor other than hexamine.

It has been mentioned that HMX is always produced in amounts ranging from 2 to 8% in the combination process. It is of interest that the process may be carried out so as to obtain good yields of a product consisting mainly of HMX[d] (contaminated by a little RDX). Since it is possible to destroy preferentially the RDX by an alkaline digestion, this constitutes an excellent synthesis of pure HMX.[19] It is also possible to obtain HMX by nitration of DPT although the evidence is clear that DPT is not an intermediate in the formation of HMX from hexamine, acetic anhydride, nitric acid, and ammonium nitrate.

In the course of these studies on the mechanism of the combination process an enormous amount of information was collected on the fundamental chemistry of hexamine, but in spite of the large amount of data collected, and the thorough study of all of the products which were obtained, the true nature of the reaction has not been discovered nor has it been possible to improve the yields over those obtained by using methods developed empirically.

1.2.2 Pilot Plant Development

It has been indicated that by the summer of 1941 work in the United States, Canada, and Great Britain showed there were three practical methods for the synthesis of RDX. The nitrolysis reaction was the first of these developed and was operated on a large scale in England and the United States in spite of the inherent disadvantages that one-half of the formaldehyde which is introduced is lost, and that large amounts of nitric acid must be handled and recovered. The Canadian method does not require nitric acid; and, at the time under consideration, the supply of acetic anhydride was not critical. The amount of acetic anhydride required in the Canadian process was such that the problem of handling liquids was less serious than in the nitrolysis process. Theoretically it should be possible by this reaction to convert all of the formaldehyde to RDX and in this way overcome the second disadvantage of the nitrolysis reaction. Studies on a pilot plant scale, confirmed in a production plant, showed, however, that this process was only slightly more economical of formaldehyde than the nitrolysis reaction. Laboratory work on the combination process indicated the possibility of obtaining 80% of the theoretical amount (2 moles) of RDX as RDX(B), thereby producing over twice as much explosive per pound of formaldehyde as was produced by the other methods. Although the process involved the recovery of acetic acid, the amount involved was about 40% of that necessary in the Canadian process, and, therefore, this method seemed the most promising of all from the standpoint of economy of formaldehyde and in economy of handling liquids for recovery.

In view of the above considerations and of the facts that the Canadian process was being studied on a pilot plant scale in Canada and that the nitrolysis process had been studied on a large scale in Britain, it was decided to conduct pilot plant studies of the combination process. At the time this decision was made, laboratory experimentation had been centered largely upon the use of hexamine dinitrate as a starting material. The first RDX(B) pilot plant, built and operated by the Western Cartridge Company, was therefore devoted to a batch process using hexamine dinitrate as a starting material.[21]

In December 1941, a study of the recovery of acetic acid from the nitration mother liquor was undertaken under a contract with the Tennessee Eastman Corporation. At this time various considerations led to a decision to undertake a study of the preparation of RDX(B) in a second pilot plant under contract with E. I. du Pont de Nemours and Company. By this time, it had been shown that hexamine was satisfactory starting material for the nitration, and the du Pont pilot plant studied a batch process based on the nitration of hexamine.[22]

Due to delays encountered in starting operations of the du Pont pilot plant and to the urgency of having waste acid for recovery studies, a contract for the construction and operation of a third RDX(B) pilot plant was negotiated in January 1942 with the Tennessee Eastman Corporation. After preliminary experimentation, it was decided that this pilot plant would use hexamine as a starting material in a continuous nitration. Since these pilot plants represented the only source of RDX in the U. S. at this time, and

[d] A 73% yield of pure HMX was obtained in one-step batch operation, and a 60% yield of pure HMX in continuous operation. Continuous operation was used for the preparation of some 25,000 pounds of HMX at the Holston Ordnance Works. The earlier alternative and much less satisfactory preparation of HMX from hexamine via DPT is described in reference 20.

since Composition B was desired for experimental purposes, the Tennessee Eastman pilot plant carried out a pilot plant study of the preparation of Composition B. The results of the Tennessee Eastman studies on acid recovery, RDX(B) preparation, and Composition B preparation are reported together.[23]

As a result of the pilot plant studies, it was decided that hexamine dinitrate would not be used as a starting material. This was due primarily to the fact that hexamine dinitrate is itself an explosive and its use represented an additional hazardous operation. Furthermore it is hygroscopic, and drying facilities would require additional construction and would be hazardous. The continuous nitration gave appreciably higher yields than the batch nitration, and the process adopted for production by the Army Ordnance Department was, therefore, the continuous process using hexamine as a starting material. The Tennessee Eastman Corporation pilot plant was transferred to the Ordnance Department in August 1942 for training personnel for the production plant. The Holston Ordnance Works of the Tennessee Eastman Corporation was designed for the production of 170 tons per day of RDX(B) by the continuous process and was later expanded to produce somewhat more than double this quantity.

1.2.3 Description of Continuous Process and Incorporation

The process as developed in the NDRC-Tennessee Eastman pilot plant was as follows. Three solutions were introduced simultaneously and equivalently into the nitrator. These solutions consisted of (1) acetic anhydride, (2) hexamine dissolved in acetic acid, and (3) ammonium nitrate in nitric acid. The nitrator used can be visualized in a simplified form as a long U tube with a tube near and connecting the upper ends of the U. Actually the U tube was built in a horizontal position and the liquid contained in it was circulated very rapidly through the tube by means of a pump. RDX(B) was formed during the circulation and the resultant slurry overflowed into a hold-up tank. After a suitable quantity of the reaction mixture had been collected, it was diluted with water to about 35 to 40% acid and heated in a simmer tank at about 95 C for approximately 1½ hours. The RDX(B) was washed and collected on a trolley filter and the wet RDX(B) dissolved in 85% acetone. The acetone was removed by distillation with steam, the slurry passed through a colloid mill, and the RDX(B) collected on a trolley filter was then added to molten TNT, with or without wax, under water. The water was removed by decantation and the slurry heated in the incorporator until the remaining water was completely vaporized. Drops of molten Composition B were allowed to fall on a continuous stainless steel belt, giving pellets resembling chocolate buds in size and shape.

1.2.4 Acid Recovery[e]

The mother liquor obtained by the filtration of the diluted reaction mixture was adjusted to pH 2.0 by the addition of alkali, in order to neutralize a small amount of excess nitric acid. Distillation in a primary still gave a nitrate-free distillate containing 30 to 40% acetic acid and a residual sludge which was discarded. It was considered that this residue from large-scale operations would be suitable for a fertilizer. The aqueous acetic acid distillate was converted to glacial acid by azeotropic distillation and converted to acetic anhydride by conventional industrial processes.

1.2.5 Refining

The various by-products which accompany RDX-(B) have been described elsewhere. With the exception of HMX, these by-products are decomposed during the simmer operation and no further refining is necessary to remove these impurities. Refining does, however, give additional assurance that BSX and related compounds are completely destroyed. Neither the simmer operation nor acetone purification removes HMX, which occurs in quantities of 3 to 8% in RDX(B). It has been pointed out earlier that HMX in no way affects adversely the quality of the product as long as only the β-polymorph is present. While the process can be operated so as to give the β-polymorph, acetone refining is an additional safeguard against the formation of sensitive HMX polymorphs. One of the important considerations in introducing acetone refining was the fact, which first became evident during pilot plant operations, that this presented a method for controlling the particle size of the product and, hence, the pourability of the Composition B derived from it. This step also decreases the acidity of the product and greatly simplifies the production of acid-free material, since occluded acetic acid is extremely difficult to remove from RDX(B) by water washing or boiling. It should, perhaps, be added that investigations by the

[e]Some work had been done earlier at the University laboratories on the problem of acid recovery.[8,24]

Holston Ordnance Works, under the auspices of the Army Ordnance Department, have indicated that in some ways cyclohexanone is superior to acetone as a solvent for refining.

1.2.6 Analytical and Test Methods

Most of the control methods are described in the reports from the pilot plants. These methods are of too limited interest to justify complete discussion in this report. Other laboratories collaborated in a number of problems concerned with control operations. An investigation was made of the melting points of samples of RDX(B) and a special apparatus for determining the melting point was designed.[25] A method was devised using a glass electrode for adjusting the *p*H of the aqueous acetic acid before primary distillation.[26] A specific conductance measurement in a special cell was recommended for measuring the concentration of water in the solution of ammonium nitrate in nitric acid which is used in the nitration.[27] A special apparatus was constructed which permitted the determination of water in RDX(B) and in Composition B in quantities as low as 0.1%. This procedure involved conductometric titration with acetic anhydride in acetic acid containing sulfuric acid.[28] Various methods were developed for the determination of HMX in RDX(B).[29] One of these methods, chromatography, requires detailed mention.

A thorough study was made of the chromatographic behavior of RDX and nine related compounds.[30,31] The primary objective was to provide a method for the analysis of production lots of RDX and RDX(B) in order to determine the significance of the melting points of the two products. It was shown that the product from the Holston Ordnance Works (combination process), although sometimes melting as low as 188 C, contained materials other than RDX and HMX to the extent of only a few thousandths of one per cent, whereas the material from the Wabash River Ordnance Works (nitrolysis process), although never melting below 200 C, contained several hundredths of one per cent of cyclonite oxide and HMX and extremely small traces of other unidentified compounds. These experiments confirmed the earlier belief that the lower melting point of the combination product was in no way a reflection of inferior quality. As a preparation for the chromatographic analysis of these plant samples, the chromatographic behavior of the compounds related to RDX, which conceivably could be by-products of either process, were investigated.

1.2.7 Special Problems

A number of problems involved in the development operation were of sufficient urgency to justify the assignment of other groups to assist the pilot plant personnel. The problem of HMX polymorphism has been discussed elsewhere in this report. The heat of reaction in the formation of RDX(B) was determined for both batch and continuous nitrations.[32] In the early pilot plant operations, difficulty was encountered in the formation of a scale on the walls of the nitrator.[33] This was shown to depend upon the heat transfer in the equipment, and it was found that the coating could be removed by heating the nitration mixture to a slightly higher temperature or by adding a mixture of acetic acid and acetic anhydride. Proper construction of the nitrator eliminated this difficulty. Small-scale experiments were performed in order to determine the hazards which might result if feeds to the nitrator were accidentally stopped.[34] Medical studies on the health hazards involved in the process indicated that these were not greater than those encountered in the manufacture of other military explosives. RDX(B) taken internally is toxic and produces in animals convulsions which may be controlled by the administration of nembutal. Contact with fumes from the nitration mixture may produce dermatitis, but no evidence was obtained of severe systemic toxicity from the manufacturing operations or from RDX(B) itself.[35] The studies were useful in making recommendations regarding health precautions in the full-scale plant.

1.2.8 Raw Materials Requirement

On the basis of pilot plant studies running continuously for twenty-eight days, the yield of RDX(B) per pound of hexamine was 2.622 lb. The production of one pound of RDX(B) required 0.39 lb of hexamine, 0.77 lb of acetic acid, 0.66 lb of ammonium nitrate, 2.05 lb of acetic anhydride, and 0.79 lb of nitric acid. In acetone refining, 0.068 lb of acetone was lost per pound of RDX(B). In neutralizing the mother liquor, 0.44 lb of sodium hydroxide was required per pound of RDX(B). Pilot plant studies of acid recovery indicated that 0.18 lb of acetic acid would be lost per pound of RDX(B) produced. In all, 148,727 lb of crude and 142,932 lb of refined RDX(B) were produced in the pilot plant. A total of 221,070 lb of Composition B was produced. It should be pointed out that, while this scale of operations gave a reasonably clear picture of the process,

the continuous operation of the large-scale plant has resulted in some modification of the above figures.

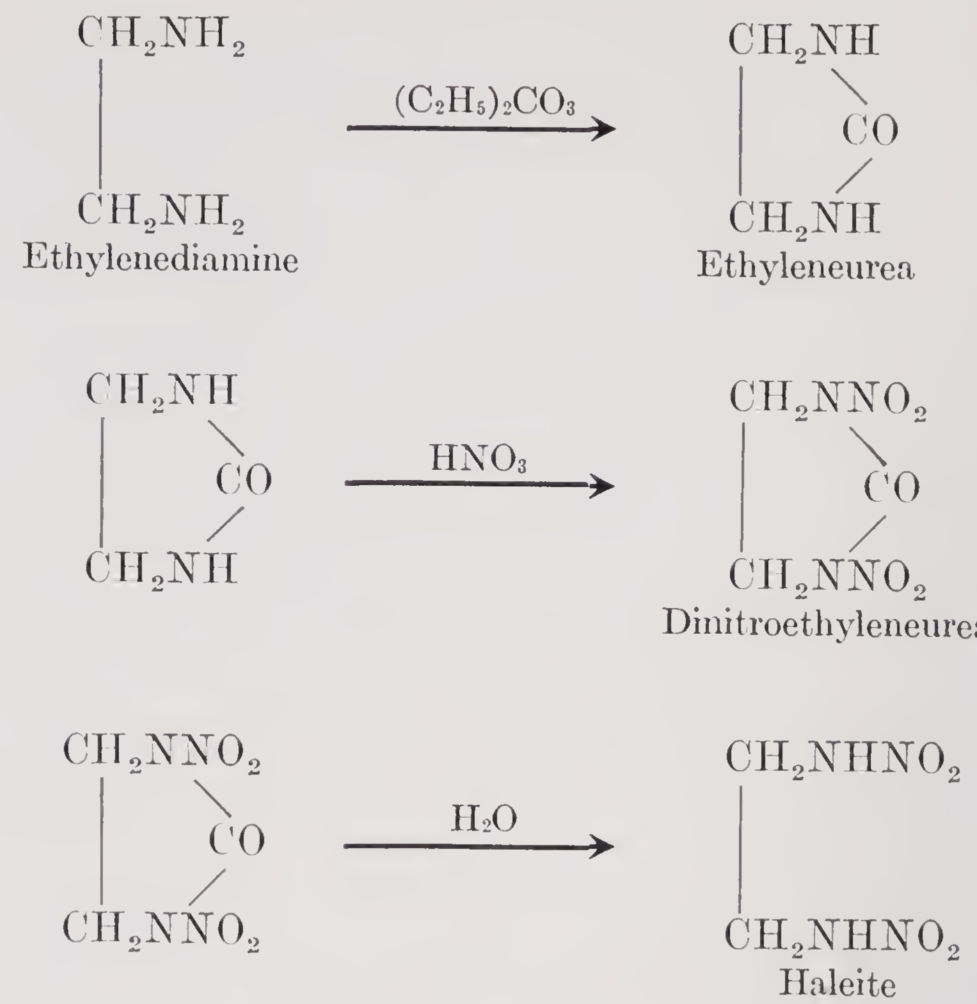
1.2.9 Comparison of Processes

The batch process studied by the du Pont Company gave a yield of 2.4 lb of RDX(B) per pound of hexamine. The raw material requirements differed very little from those of the continuous process, and it should be emphasized that it is perfectly feasible to prepare RDX(B) by batch operations. Although the continuous process has some advantages, it is easy to visualize a situation in which availability of equipment might justifiably lead to a decision to use batch operations in preference to continuous.

The comparison of 2.62 lb of RDX(B) per pound of hexamine by the continuous process with 1.17 lb of RDX by the conventional process probably appears more favorable than is actually warranted. In general, it seems probable that the combination process would be the preferred one. In time of war ammonia oxidation units and equipment for methanol and ammonia are likely to be in great demand. Since the combination process requires much less nitric acid, less formaldehyde, and less ammonia than the nitrolysis, it would be preferred unless acetic acid, acetic anhydride, and the equipment for manufacturing these were in critical condition. Since 98% nitric acid can be made and the oxide and dilute acid from the nitrolysis process can be recovered quite cheaply, a competitive demand for acetates might make the nitrolysis process the logical one for large-scale operations. The differences in cost of the product are probably less decisive than the availability of equipment and raw materials in determining the method to be used for the production of RDX.

1.3 HALEITE[f]

The first investigation in this country of the preparation and explosive properties of ethylenedinitramine, officially designated as Haleite by the Services,[g] was begun at the Picatinny Arsenal about 1933. Haleite was prepared from ethylenediamine by the following three-step process.



This process suffers from two disadvantages: the overall yield is only 42% of the theoretical amount; and the initial step, the reaction between ethylenediamine and ethyl carbonate, requires the use of high pressures and temperatures over an extended period of time. However, the explosive properties of Haleite were of sufficient interest to lead to the recommendation by the Picatinny Arsenal that further work should be done on the preparation of the material, and it was indicated that Haleite would be of great military interest if it could be prepared for 50 cents or less per pound.

With this background Division 8 began work in the fall of 1940 on the synthesis of Haleite. Since assurances had been received that ethylenediamine could be purchased in quantities as large as 40 tons per day at a cost of 25 cents per pound, the work was directed toward a synthesis of Haleite that would avoid the unsatisfactory step in the Picatinny Arsenal process —the preparation of ethyleneurea from ethylenediamine and ethyl carbonate. Two approaches were investigated: the first was a synthesis of Haleite that did not involve ethyleneurea as an intermediate; the second was an improved synthesis of ethyleneurea from ethylenediamine.

Laboratory studies showed that ethylenediamine reacted smoothly with ethyl chloroformate at 80 C and at atmospheric pressure to form the dicarbethoxy derivative (I). Nitration of (I) and subsequent hydrolysis of the nitration product furnished Haleite in an overall yield of 87% based on ethylenediamine

[f]This section is based on a summary prepared by S. R. Aspinall.

[g]The name Haleite was given to ethylenedinitramine by Ordnance Committee Item 40,757 of June 17, 1943. Prior to this action the substance was referred to as EDNA.

$$\begin{array}{l} \mathrm{CH_2NH_2} \\ | \\ \mathrm{CH_2NH_2} \end{array} \xrightarrow{\mathrm{ClCO_2C_2H_5}} \begin{array}{l} \mathrm{CH_2NHCO_2C_2H_5} \\ | \\ \mathrm{CH_2NHCO_2C_2H_5} \end{array} \xrightarrow{\mathrm{HNO_3}}$$

(I)

$$\begin{array}{l} \mathrm{CH_2N(NO_2)CO_2C_2H_5} \\ | \\ \mathrm{CH_2N(NO_2)CO_2C_2H_5} \end{array} \xrightarrow{\mathrm{H_2O}} \begin{array}{l} \mathrm{CH_2NHNO_2} \\ | \\ \mathrm{CH_2NHNO_2} \end{array}$$

An alternative procedure utilizing diacetylethylenediamine (II) as an intermediate was also developed. This procedure gives a 76% yield of Haleite.

$$\begin{array}{l} \mathrm{CH_2NH_2} \\ | \\ \mathrm{CH_2NH_2} \end{array} \xrightarrow{\mathrm{(CH_3CO)_2O}} \begin{array}{l} \mathrm{CH_2NHCOCH_3} \\ | \\ \mathrm{CH_2NHCOCH_3} \end{array} \xrightarrow{\mathrm{HNO_3}}$$

(II)

$$\begin{array}{l} \mathrm{CH_2N(NO_2)COCH_3} \\ | \\ \mathrm{CH_2N(NO_2)COCH_3} \end{array} \xrightarrow{\mathrm{H_2O}} \begin{array}{l} \mathrm{CH_2NHNO_2} \\ | \\ \mathrm{CH_2NHNO_2} \end{array}$$

Neither of these processes was put into pilot plant operation.[36,37]

Two methods were developed for the conversion of ethylenediamine to ethyleneurea.[38-41]

1. Ethylenediamine and carbon dioxide heated at 220 C and 820 atm for 30 minutes furnish ethyleneurea;

$$\begin{array}{l} \mathrm{CH_2NH_2} \\ | \\ \mathrm{CH_2NH_2} \end{array} \xrightarrow{\mathrm{CO_2}} \begin{array}{l} \mathrm{CH_2NH} \\ |\qquad \diagdown \\ |\qquad\quad \mathrm{CO} \\ |\qquad \diagup \\ \mathrm{CH_2NH} \end{array}$$

but this synthesis, like that from ethylenediamine and ethyl carbonate, requires high temperatures and pressures and does not give an outstandingly high yield.

2. Ethylenediamine and urea heated in aqueous solution at atmospheric pressure furnish ethyleneurea in quantitative yield.

$$\begin{array}{l} \mathrm{CH_2NH_2} \\ | \\ \mathrm{CH_2NH_2} \end{array} + \mathrm{NH_2CONH_2} \longrightarrow \begin{array}{l} \mathrm{CH_2NH} \\ |\qquad \diagdown \\ |\qquad\quad \mathrm{CO} \\ |\qquad \diagup \\ \mathrm{CH_2NH} \end{array} + 2\mathrm{NH_3}$$

The ammonia evolved can be treated with carbon dioxide and reconverted to urea.

The procedures outlined above provided satisfactory syntheses of Haleite starting from ethylenediamine. However, at this stage in the work it was learned that the earlier assurances of an adequate supply of ethylenediamine at a price of 25 cents per pound were in error; and that ethylenediamine would be available only at a price of more than 50 cents per pound. This made it necessary to develop either a synthesis of ethyleneurea which did not involve ethylenediamine or a synthesis of ethylenediamine itself.

A synthesis of ethyleneurea from ethylene glycol was first worked through.[38,42,43]

$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CH_2OH} \end{array} + \mathrm{NH_2CONH_2} \longrightarrow \begin{array}{l} \mathrm{CH_2\text{-}NH} \\ |\qquad \diagdown \\ |\qquad\quad \mathrm{CO} \\ |\qquad \diagup \\ \mathrm{CH_2\text{-}NH} \end{array} + 2\mathrm{H_2O}$$

In practice this reaction takes place in two steps. One mole of ethylene glycol is heated at atmospheric pressure for ten hours with five moles of urea. The product is an ethyleneurea polymer which, on heating with water, furnishes ethyleneurea. The four moles of excess urea are hydrolyzed to ammonia and carbon dioxide, but the ammonia can be reconverted to urea. Since at the time the process was under study there was ample unused urea capacity available, this was a serious, but not a fatal, disadvantage. Consequently the process was put through pilot plant trials. From these trials it was estimated that a plant capable of producing 10 tons per day of ethyleneurea at a cost of 45 cents per pound could be built for $1,000,000, and a plant capable of producing 60 tons per day at a cost of 40 cents per pound could be built for $4,000,000.

Attention was next turned to the development of a synthesis of ethylenediamine. The successful synthesis consists of the following steps.

$$\mathrm{CH_2O} + \mathrm{HCN} \longrightarrow \mathrm{HOCH_2CN} \quad (98\%\ \text{yield})$$

$$\mathrm{HOCH_2CN} + \mathrm{NH_3} \longrightarrow \mathrm{H_2NCH_2CN} + \mathrm{H_2O} \quad (82\%\ \text{yield})$$

$$\mathrm{H_2NCH_2CN} + 2\mathrm{H_2} \longrightarrow \mathrm{H_2NCH_2CH_2NH_2} \quad (88\%\ \text{yield})$$

The raw materials used in this process are cheap and available; the reactions proceed smoothly, rapidly, and in good yields; only the third step, the hydrogenation, requires high pressures. Since the hydrogenation is a continuous rather than a batch operation, it presents no serious difficulties in the way of equipment requirements. The process was, therefore, put into pilot plant operation where it produced ethylenediamine in 70% overall yield.[40,41]

It will be recalled that two methods had been studied earlier for converting ethylenediamine to ethyleneurea: the reaction with urea, and the reaction with carbon dioxide. The former had been selected as the more satisfactory. Since that time further work on the ethylenediamine-carbon dioxide reaction, done by the Ralph L. Evans Associates under contract with the Ordnance Department, had shown that this reaction could compete favorably with the ethylenediamine-urea process. A pilot plant study of the ethylenediamine-carbon dioxide reaction was made, and operating conditions were worked out whereby this reaction became the most satisfactory one for the preparation of ethyleneurea.[44-47]

All the work described so far can be summarized as leading to the following preferred total synthesis of Haleite:

$$CH_2O + HCN \longrightarrow HOCH_2CN$$

$$HOCH_2CN + NH_3 \longrightarrow H_2NCH_2CN + H_2O$$

$$H_2NCH_2CN + 2H_2 \longrightarrow H_2NCH_2CH_2NH_2$$

$$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2NH_2 \end{array} + CO_2 \longrightarrow \begin{array}{l} CH_2\text{-}NH \\ | \qquad \rangle CO \\ CH_2\text{-}NH \end{array} + H_2O$$

$$\begin{array}{l} CH_2NH \\ | \qquad \rangle CO \\ CH_2NH \end{array} + 2HNO_3 \longrightarrow \begin{array}{l} CH_2NNO_2 \\ | \qquad \rangle CO \\ CH_2NNO_2 \end{array} + 2H_2O$$

$$\begin{array}{l} CH_2NNO_2 \\ | \qquad \rangle CO \\ CH_2NNO_2 \end{array} + H_2O \longrightarrow \begin{array}{l} CH_2NHNO_2 \\ | \\ CH_2NHNO_2 \end{array} + CO_2$$

Taking advantage of improvements in the nitration of ethyleneurea, achieved by using nitric acid alone instead of mixed acid,[46] this synthesis permits the preparation of Haleite at a cost of about 30 cents per pound.

In addition to the work described up to this time, Division 8 supported one laboratory investigation of an entirely different synthesis of ethylenediamine. The National Research Council in the fall of 1941 canvassed chemists in this country for suggestions for new syntheses of ethylenediamine. Seventeen different methods were suggested, and the chemists who proposed them did some preliminary work on a volunteer basis. One proposed method—the addition of nitrogen dioxide to ethylene followed by reduction of the addition product, 1,2-dinitroethane, to ethylenediamine—was considered to be of sufficient interest to merit study by Division 8. The study showed that the addition of nitrogen dioxide to ethylene gave only a moderate amount of material reducible to ethylenediamine, and that the addition reaction would be cumbersome and hazardous to apply to large-scale operation.[48-50]

Finally, in view of the important results obtained in the study of the crystallography of RDX and related compounds (see Section 1.2), a comparable study was made of Haleite. No polymorphs were found, but information of importance in securing pellets of high density was obtained.[51]

1.4 DINA[h]

About September 1942 it was discovered in Canada that the conversion of a secondary amine nitrate to the corresponding nitramine (the Bamberger reaction) takes place efficiently in the presence of chloride ion. This discovery made it possible to prepare *bis*-β-nitroxyethylnitramine, DINA,[i] from diethanolamine, nitric acid, acetic anhydride, and a trace of an ionic chloride. The preparation of DINA was investigated on a pilot scale in Canada and extensive tests of its properties as a high explosive were made in Canada and in this country. The low melting point, relative chemical instability and sensitivity to impact under certain conditions militated against serious consideration of DINA as a high explosive in spite of its excellent power, but it became apparent by the middle of 1943 that this explosive showed great promise as an ingredient of propellants. A discussion of the use of DINA in gun propellants of superior qualities is given under Albanite (Section 6.7); the present section deals exclusively with the preparation of DINA itself.

The preparation of DINA[j] by nitration of diethanolamine may be carried out by a two-step or a one-step procedure. In the two-step procedure diethanolamine is slowly added to a slight excess of concentrated nitric acid; the resulting solution, which consists of diethanolamine trinitrate (and some lower nitrates of diethanolamine) dissolved in nitric acid, is then fed slowly into a slight excess of acetic anhy-

[h]This section is based on a summary prepared by S. R. Aspinall.

[i]Key references to the properties of DINA as a high explosive are given in reference 52.

[j]The complete record of the investigations on the preparation of DINA and the associated problems referred to later in this section is to be found in references 53–58.

dride containing catalytic amounts of chloride ion. The nitration mixture is drowned, the precipitated DINA removed by filtration and washed with water. In the one-step nitration the appropriate amounts of diethanolamine and nitric acid are fed simultaneously (with a nitric acid lead) into acetic anhydride containing chloride ion. After completion of the reaction the mixture is drowned and treated as before. Because of the advantages of the one-step nitration from the standpoints of simplicity of operation and economy of equipment and because results obtained with it were at least as good as those from the two-step procedure, only the one-step process was evaluated on a pilot scale.

It is necessary to purify the crude crystalline DINA obtained by either process, since it contains residual acidity and appreciable amounts of the corresponding nitrosamine which lower the stability of the product. The purification procedure consists essentially of treating DINA with hot water with vigorous agitation. This treatment results in the destruction of the nitrosamine, which is very unstable at the temperatures encountered, and the extraction of the residual acid into the aqueous phase. The molten pure DINA resulting from this treatment is allowed to settle and is drawn off to be crystallized under cold water or from an appropriate solvent. However, because of the extreme sensitivity of DINA under certain conditions, especially when molten,[59] the purification of DINA in quantity as outlined above was not looked upon with favor. Therefore, on a pilot scale the crude crystalline DINA was mixed with dibutyl phthalate and centralite in the ratio 88.5 : 10 : 1.5, and the resulting mixture heated with hot water as before. The aqueous layer was neutralized to destroy acidity extracted from the DINA, and the DINA-dibutyl phthalate-centralite mixture (called DDP) allowed to settle, after which it was drawn off into small drums where it solidified to a superficially dry cast. This modification in purification was permissible because dibutyl phthalate and centralite are ingredients of Albanite, into which the DINA was converted, and offered great advantages from the standpoint of production and storage because of the strong phlegmatizing action of the dibutyl phthalate and the stabilizing action of the centralite.

The waste acid filtered from the crude DINA consists of 30% acetic acid containing small amounts of nitric acid, hydrochloric acid, DINA, and organic by-products arising from diethanolamine and the impurities present in it (chiefly mono- and triethanolamines). The waste acid is simmered to hydrolyze organic nitrates and is partially neutralized with caustic to fix the mineral acids. The waste thus treated may be extracted continuously with isopropyl or ethyl ether and the extract fractionated to yield nitrate- and chloride-free glacial acetic acid suitable for conversion to acetic anhydride. Alternatively the simmered waste may be distilled to yield chloride- and nitrate-free 30% acetic acid which is then distilled azeotropically to give glacial acetic acid suitable for conversion to acetic anhydride.

A number of problems associated with the DINA process were investigated. The results are mentioned briefly in the following paragraphs.

Quality of Raw Materials

A method was developed for the analysis of diethanolamine. Adequate methods for analyzing nitric acid and acetic anhydride were already known. These methods are useful for plant control, but are not vitally important to the process, since it was shown that the yield and quality of DINA were as satisfactory with standard commercial materials as with specially purified ones.

Catalyst

Many materials have been evaluated as catalysts for the nitration, but none worked so well as chloride ion. Hydrogen chloride is favored for plant use because of its cheapness and the fact that no metal is introduced into the reaction.

An attempt was made to demonstrate the exact mode by which chloride ion functions as a catalyst, but no conclusive results were obtained.

By-Products

A study was made of the preparation and properties of the possible by-products in the DINA synthesis. The most important are those arising from diethanolamine and consist of the nitrosamine analog of DINA, (*bis*-β-nitroxyethylnitrosamine), and the analogs of DINA in which one or more of the nitro groups are replaced by acetyl groups.

The nitrosamine occurs in crude DINA, but it is eliminated in the purification with hot water, since the rate of hydrolysis of the nitrosamine to water-soluble products is extremely rapid as compared to the rate of hydrolysis of DINA.

The mixed nitro-acetyl derivatives of diethanolamine have never been positively demonstrated to be present in crude DINA. Certain of these compounds undergo rearrangement in the presence of water to

give water-soluble ammonium nitrate derivatives. The following equation is illustrative.

$$\left.\begin{array}{l}O_2NOCH_2CH_2\\O_2NOCH_2CH_2\end{array}\right\rangle NCOCH_3 + H_2O \longrightarrow \left.\begin{array}{l}CH_3CO_2CH_2CH_2\\O_2NOCH_2CH_2\end{array}\right\rangle NH_2NO_3$$

Certain other of these compounds, if formed at all, are sufficiently soluble or unstable in the waste acid that they do not occur in crude DINA. That these mixed nitro-acetyl derivatives are formed initially in the reaction is evidenced by the fact that yields of DINA from diethanolamine are less than those from *bis*-(β-nitroxyethyl)ammonium nitrate and also by the fact that certain of the compounds or their degradation products are found in the waste acid.

MISCELLANEOUS

Many variations of the hot-water treatment were tried, including the addition of various reagents which might improve the stability of refined DINA. The only additive which accomplished an improvement in stability and which was acceptable from the standpoint of powder manufacture was centralite.

Chromatography has been used to prepare very pure samples of DINA. It was shown that DINA stabilized by the usual methods contains extremely small quantities of impurities, and that such DINA is as stable as judged by accepted stability tests as chromatographically pure DINA.

Extensive data were obtained on the solubility and crystallographic properties of DINA and on the phase behavior of the system DINA-centralite. Absorption spectra of DINA and related compounds have been measured; the data obtained have been useful in evaluating the quality of the nitration product.

1.5 MISCELLANEOUS NITRAMIDES, NITRAMINES, AND NITRAMINE-NITRATE ESTERS[k]

The excellent explosive properties of the cyclic nitramine RDX prompted an investigation of a wide variety of compounds containing the NNO_2 group. In part this work had as its object the preparation of nitramines which might be useful as explosives; in part it was intended as an exploration of the chemical behavior of compounds containing the NNO_2 group. Nitramides, nitramines, and compounds containing both nitramine and nitrate ester groups were studied. The most important compounds, Haleite, a high explosive, and DINA, an explosive plasticizer for gun propellants, have been discussed in Sections 1.3 and 1.4 respectively; the remaining compounds are discussed in the paragraphs which follow.

1.5.1 Nitramides

Nitramides have been prepared by direct nitration of the following classes of compounds: hydantoins, diketopiperazines,[60] glycolurils,[36,61] melamine and its triacetyl derivative,[62,63] N-substituted oxamides,[64-65] N-substituted glycolamides, substituted ureas, hydantoic acid derivatives, and sulfamides. Attempts to prepare nitro derivatives of hexahydro-*s*-triazinones and *bis*-(2-hydroxyethyl) urea were unsuccessful.

The nitramides as a class were found to be unsuitable for use as military explosives. Their stability toward moisture and heat was inadequate. The nitro derivatives of the hydantoins and diketopiperazines are markedly hygroscopic.

1.5.2 Nitramines

Both primary and secondary nitramines were prepared and examined. Preparation of primary nitramines usually involves a procedure developed by Franchimont and Klobbie.[66]

$$RNH_2 \xrightarrow{ClCO_2C_2H_5} RNHCO_2C_2H_5 \xrightarrow{HNO_3} RN(NO_2)CO_2C_2H_5 \xrightarrow{NH_3} RNHNO_2$$

Preparation of secondary nitramines either involves the alkylation of primary nitramines or the catalyzed dehydration of secondary amine nitrates.[67]

$$R_2NH_2NO_3 \xrightarrow{Ac_2O\,+\,Cl^-} R_2NNO_2$$

Among the simple aliphatic nitramines prepared were a number of nitramino analogs of well-known nitrate ester explosives: 1,2-dinitraminopropane, 1,2,3-trinitraminopropane, and pentaerythrityl tetranitramine, the nitramine analogs of propylene glycol dinitrate, nitroglycerin, and PETN.[37,68] From the studies of these and other related nitramines it may be concluded that they, in comparison with the nitrate esters, are more stable toward heat, less sensitive to impact, somewhat less powerful, much higher melting, and much more difficult to prepare.

Details of the preparation, properties, and reactions of the various nitramines are to be found in the ref-

[k] This section has been constructed from information furnished by A. T. Blomquist.

erences already cited. Only three other lines of activity can be mentioned in detail here.

Attempts to prepare polynitramines from diethylenetriamine, $H_2NCH_2CH_2NHCH_2CH_2NH_2$ and triethylenetetramine, $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, were only partially successful.[69-71]

Studies of the ultraviolet absorption spectra of several primary nitramines and their salts and of the isomers, trimethylolmethylnitramine and N-trimethylolmethyl-N-nitrosohydroxylamine, aided in proving that the product obtained from acetone by the Traube reaction was not methylenedinitramine,[1] as it had long been believed to be, but was, instead, methylene-*bis*-nitrosohydroxylamine.[72]

Preliminary studies were made of N-halogenated derivatives of primary aliphatic nitramines. The compounds prepared were thermally unstable and quite sensitive to impact.[68]

1.5.3 Nitramine-Nitrate Esters

As part of the work on explosive plasticizers for Albanite powder (see Section 6.7), a number of nitramine-nitrate esters were prepared and evaluated. Those containing a primary nitramino group, (NENA, $O_2NOCH_2CH_2NHNO_2$, is an example) were prepared from aminoalcohols by the procedure outlined above for primary nitramines. Those containing one or more secondary nitramino groups were prepared either by the catalytic dehydration of the amine nitrates of the appropriate aminoalcohols or by alkylating a primary nitramine, such as ethylenedinitramine, with an alkylene oxide.[53]

The two last-named procedures led to three groups of nitramine-nitrate esters:[74a,b,75]

1. DINA analogs, $(O_2NOCH(R)CH_2)_2NNO_2$.
2. N-Alkyl analogs of NENA, $(O_2NOCH(R)CH_2$-$N(R)NO_2$.
3. Compounds derived from ethylenedinitramine.

$$O_2NOCH(R)CH_2\underset{}{\overset{\overset{NO_2}{|}}{N}}CH_2CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH(R)ONO_2$$

Of the nitramine-nitrate esters prepared in these ways, DINA, butylNENA, cyclohexylNENA, and, perhaps, *bis*(2-nitroxyethyl)ethylenedinitramine have shown the most promise as explosive plasticizers. The nitramine-nitrate esters as a class are not so satisfactory as RDX or Haleite for use as high explosives.

[1] The true methylenedinitramine had been obtained in an entirely different way by British workers.[73]

1.6 ALIPHATIC AND AROMATIC NITRO COMPOUNDS[m]

1.6.1 Aliphatic Nitro Compounds

Recent industrial developments have made several simple nitroparaffins commercially available. These volatile, liquid nitroparaffins are not themselves suitable as military high explosives. They have been used, however, as starting materials for the preparation of more complex polynitroparaffins which might reasonably be expected to have military applications. In this synthetic program a number of previously known polynitroparaffins were made by improved techniques and some new compounds were made by well-established methods.[n] None of the compounds prepared was of immediate interest. Those compounds which were promising could not be prepared by a practical procedure. Those compounds which could be prepared with any facility were disqualified as high explosives for one or more of the following reasons: (1) low melting point or high vapor pressure, (2) insufficient power, (3) lack of stability, (4) acidity due to the presence of α-hydrogen atoms.

Much time was spent on unsuccessful efforts to synthesize tetranitroneopentane, $C(CH_2NO_2)_4$, and 2, 2, 5, 5-tetranitrohexane, $CH_3C(NO_2)_2CH_2CH_2C(NO_2)_2CH_3$. From the difficulties encountered in these attempts and in less extensive efforts on related compounds, it is a reasonable prediction that the development of satisfactory syntheses of polynitroparaffins suitable for use as military high explosives will be a long-term project dependent for its success on a very considerable increase in our knowledge of the chemistry of the simple nitroparaffins and their derivatives.

Three simple polynitroparaffins have received some attention in the laboratory. Nitroform (trinitromethane) was prepared by procedures described in the literature, and some of its reactions were explored in preliminary fashion; the condensation with formaldehyde to furnish trinitroethanol was successful.[78] Tetranitromethane was also prepared by methods available in the open literature.[79] The preparation of 1,2-dinitroethane from ethylene and nitrogen dioxide was investigated rather carefully; the maximum conversion was 35%. 1,2-Dinitroethane was of interest not

[m] This section is constructed from material furnished by S. R. Aspinall, Marvin Carmack, and Frank H. Westheimer.

[n] The reader is referred to the original reports for the names of the large number of compounds prepared.[76,77]

in itself but as an intermediate in the preparation of Haleite (see Section 1.3).

Nitroethylene polymer was also prepared (see Section 1.8). Its explosive properties are very inferior.

1.6.2 Aromatic Nitro Compounds

Work with the aromatic nitro compounds has dealt both with preparative procedures for individual compounds and with the mechanism of the preparative reactions.

Attempts to improve the preparation of trinitrobenzene (TNB) did not lead to useful results. The synthesis of TNB from furoic acid, via mucobromic acid and nitromalonic aldehyde, was re-examined. Although the yield in the first reaction was improved, the yields in the second and third reactions could not be increased and the overall yield was only about 5%.[o] A successful laboratory procedure was developed for converting picryl chloride to TNB by reducing the chloride in aqueous alcoholic solution with copper powder. The yield of TNB is 77%, and the copper can be recovered and used again. An alternative procedure, the hydrolysis of trinitrobenzenesulfonic acid, did not work.[81]

A process for the nitration of benzene and toluene in the absence of sulfuric acid was examined. In this process, water initially present or formed in the reaction is removed by azeotropic distillation. The economies claimed for the process were not realized in the trials.[82] Another process envisaged for the nitration of aromatic compounds in the absence of sulfuric acid involved the use of concentrated perchloric acid as the reaction medium. Work toward this end was limited to an attempt to devise an analytical method for determining the extent of nitration of samples of reactants sufficiently small to permit the safe use of concentrated perchloric acid. A micro-Kjeldahl procedure gave satisfactory results with mixtures of known composition but failed when it was applied to rate studies.[83] A study of the kinetics of nitration of nitrobenzene, dinitroxylene, dinitromesitylene, and other aromatic nitro compounds dissolved in sulfuric acid showed that the reaction between nitric acid and nitro compound was second order, and that the rate constant depended on the sulfuric acid concentration.[84] This constant is a maximum for solutions containing about 90% sulfuric acid; it is only one-sixth as great in 100% sulfuric acid and less than one-thousandth as great in 80% acid. Added materials, such as sodium bisulfate, affect the rate in the way which would be predicted from their effect on the acidity of the medium. Large quantities of nitric acid affect the acidity of the medium so as to make it approach the optimum for nitration. The position of the maximum rate is only slightly dependent on the temperature. The introduction of a nitro group into the aromatic nucleus decreases the rate of nitration by a factor of about 10^8.

Presumably the mechanism of nitration involves a reaction between the substance to be nitrated and the NO_2^+ ion. It has been shown by an indicator method that the tremendous difference in nitration rates when 80 and 90% sulfuric acid solutions are used is due to the change in concentration of the ionic intermediate, NO_2^+. Since the formation of NO_2^+ from the nitric acid controls the nitration rate, the maximum rate should and does occur at the same concentration of sulfuric acid in the nitration of nitrobenzene, 4,6-dinitro-1,3-xylene, and dinitromesitylene.

Solubility effects restrict somewhat the application of these conclusions to the large-scale preparations of aromatic nitro compounds.

The conclusions reached in the report just reviewed were confirmed by a study of the preparation of trinitroethylbenzene (TNEB).[85] Ethylbenzene was nitrated quantitatively to dinitroethylbenzene. The rate of nitration of dinitroethylbenzene to TNEB is affected by the same factors which were found to be operative in the analogous aromatic nitrations described above. The maximum yield of TNEB was 80%. The principal cause of loss was oxidation of dinitroethylbenzene by nitric acid. No method of decreasing this loss was discovered.

The preparation of the polynitronaphthalenes was studied in some detail because of the availability of naphthalene as a raw material. If it were possible to nitrate naphthalene economically to furnish explosives comparable with TNT, these products would constitute a welcome wartime addition to the supply of high explosives. Since the power of 1,3,8-trinitronaphthalene in the ballistic mortar is only 83% of that of TNT, while the power of 1,3,6,8-tetranitronaphthalene is 101% of that of TNT, it is essential to be able to nitrate naphthalene to tetranitro derivatives if the products are to be useful.

Methods were first developed for the preparation of pure trinitronaphthalenes, then the nitration of the pure trinitro compounds was studied. With the information thus obtained, procedures were developed for

[o] Unsuccessful attempts to prepare TNB from β-nitroethanol and from nitroacetaldoxime are described in reference 80.

preparing tetranitronaphthalenes from 1-nitronaphthalene, mixtures of dinitronaphthalenes, or mixtures of trinitronaphthalenes. These procedures unfortunately do not hold much practical promise, for the yield of tetranitronaphthalenes never exceeds 50%, and an excess of 3 to 4 moles of nitric acid over the amount theoretically necessary is always consumed in the process. The two disadvantages are apparently causally connected: the low yield of tetranitronaphthalenes is a result of loss by oxidation reactions, and the high consumption of nitric acid is a result of its use as the oxidizing agent in these reactions.

The following preparative procedures were developed. The yield is given in parentheses following the name of the product.

Naphthalene to 1-nitronaphthalene (94 to 98%).

1 - Nitronaphthalene to 1, 5 - dinitronaphthalene (30%) and 1,8-dinitronaphthalene (30%); yield of mixed dinitronaphthalenes, 95%.

1 - Nitronaphthalene to 1,3,8 - trinitronaphthalene (33%); yield of mixed trinitronaphthalenes, 94%.

1,5-Dinitronaphthalene to 1,4,5-trinitronaphthalene (41%); yield of mixed trinitronaphthalenes, 94%.

1,5 - Dinitronaphthalene to 1,4,5,8-tetranitronaphthalene (34%) and 1,3,5,8 - tetranitronaphthalene (14%).

1,3,8-Trinitronaphthalene to 1,3,6,8-tetranitronaphthalene (50%) and 1,3,5,8 - tetranitronaphthalene (3%).

1,4,5-Trinitronaphthalene to 1,4,5,8-tetranitronaphthalene (36%) and 1,3,5,8-tetranitronaphthalene (13%).

1-Nitronaphthalene to a mixture of tetranitronaphthalenes (50%).

Methods of separation and analysis of the nitration products were worked out; some addition compounds of 1,3,8-tritronaphthalene, and 1,3,5,8- and 1,3,6,8-tetranitronaphthalene are described; and the behavior of 1,8-dinitronaphthalene, 1,3,8-trinitronaphthalene, and 1,3,6,8-tetranitronaphthalene toward fuming sulfuric acid is reported.[86]

1.6.3 Oxynitration of Benzene to Picric Acid

The direct conversion of benzene to picric acid,[p] usually referred to as the oxynitration of benzene, has been studied both as a preparative procedure and with respect to the mechanism of the reactions involved. The work was undertaken in the fall of 1942 when it appeared that there might be a shortage of phenol for the preparation of picric acid and, from it, ammonium picrate.[q] The work was successful in that procedures were developed for the direct conversion of benzene to picric acid which are at least as efficient as, and probably more efficient than, either the nitration of phenol or the indirect preparation of picric acid from benzene via chlorobenzene; and the mechanism of the reactions involved is well understood. The process was never put into commercial operation, as the phenol shortage which had been feared did not occur. However, the process has been developed to the extent that it must be considered as a serious potential rival to the alternative processes and, before any expansion of dinitrophenol on picric acid production is undertaken, the oxynitration process should be evaluated in the pilot plant.

The oxynitration of benzene and other aromatic hydrocarbons was discovered and patented by Wolffenstein and Böters in 1906.[89] Their procedure involved the treatment of benzene with aqueous nitric acid containing mercuric nitrate. Although much attention has been devoted to the oxynitration procedure almost since its original disclosure, it was only with the work of Division 8 that the method was developed to the point where it could compete with alternative processes. In describing this work we shall, first, discuss the preparative procedures and then discuss the mechanism of the reactions involved.[90]

A critical study was made of the effects of the numerous variables, including acid strength, rate of addition of benzene (effective benzene concentration), concentration of mercuric nitrate, temperature, time, effect of nitrogen oxides, and effects of other added substances.

The two variables of greatest importance are the concentration of nitric acid and the effective concentration of benzene (that is, benzene dissolved in the oxynitration solution). The optimal concentration of nitric acid is in the range 10.4 to 11.6 M (or the equivalent of 50 to 55% by weight for pure acid). The acid concentration greatly influences the overall rate of reaction; below 10.4 M the rate falls off rapidly, while above 10.4 M the rates of both the oxynitration reaction and various side reactions, such as direct nitration, increase rapidly. The range mentioned above seems in general to give the lowest proportion of

[p]In practice the principal product of the process is either dinitrophenol or picric acid according to the experimental conditions employed.

[q]Earlier, a Canadian[87] procedure for the oxynitration of benzene by treatment with nitric acid together with mercuric, manganese, and aluminum nitrates was checked. The yield of picric acid was 50%.[88]

neutral nitro compounds to nitrophenols with, at the same time, an adequate rate of oxynitration. It is essential to fortify the oxynitration solution at frequent intervals or, preferably, continuously. Fortification with 95 to 98% nitric acid is particularly advantageous since it results in a smaller increase in reaction volume than does the use of more dilute acid; the use of absolute nitric acid does not require any special modifications of procedure except avoidance of direct contact of the strong acid with liquid benzene.

The effective benzene concentration is probably the most critical variable affecting the proportion of neutral nitro compounds to nitrophenols and also the formation of colored by-products. Vigorous agitation of excess benzene, keeping the oxynitration solution nearly saturated with benzene, leads to poor yields of nitrophenols, high yields of nitrobenzene and dinitrobenzene, and the formation of highly colored impurities which are difficult to remove from the products. In batch runs it was found that the results differ greatly if all the benzene is added in one portion or if it is added slowly over a considerable period. The yields of nitrophenols increase sharply, then level off and become constant as the time of dropwise addition of benzene is increased. The addition of small slugs of benzene at regular intervals was found to be as satisfactory as continuous dropwise addition, provided the rate of addition is carefully adjusted so as not to exceed the optimum rate of oxynitration for the particular set of conditions. In a vigorously stirred solution the benzene concentration is certainly determined very largely by the rate of conversion of benzene to intermediates; in batch runs, therefore, the rate of addition of the benzene is the important variable to control, and an excess of undissolved benzene must be avoided.

In runs with moderate stirring and an excess of benzene phase, the degree of agitation becomes a variable, since it partially determines the rate at which benzene dissolves in the oxynitration solution. The mere presence of a separate benzene phase is not in itself deleterious except when the dispersion of the benzene phase through the aqueous acid solution is such that the oxynitration solution is kept nearly saturated at all times. Good yields have been obtained in runs in which a benzene phase floated upon an unstirred reaction mixture. In the continuous extraction process to be described later a considerable amount of liquid benzene is always present but is dispersed in the form of droplets which rise rapidly through the oxynitration solution, dissolving to some extent but not necessarily rapidly enough to saturate the solution. When benzene is injected into an unstirred oxynitration solution by a device such as a fritted disk or through capillary tubes, the size of the dispersed droplets as well as the rate of addition of benzene become important variables affecting the yields and ratios of products.

The concentration of mercuric nitrate catalyst affects the rate of oxynitration, the rate being approximately proportional to the catalyst concentration when other factors are constant. Over a fairly wide range, the catalyst concentration does not appear to be a critical variable. Concentrations of 0.37 to 0.5 mole of mercuric nitrate per liter of oxynitration solution have been found to give satisfactory results in most cases.

The reaction temperature does not appear to be a critical variable except as it affects the relative rates of the various reactions. A higher proportion of nitrobenzene may be formed at higher temperatures. The overall rate of oxynitration increases by a factor of about 1.8 to 2 for each 10 C rise in temperature. At the boiling point of the oxynitration mixture, the nitration of DNP to PA gives only about an 80% yield; it is therefore obviously an advantage to isolate DNP under relatively mild oxynitration conditions, then to nitrate that product separately in a nitric-sulfuric acid mixture when the yield of PA exceeds 95%.

The presence of some nitrogen oxides is essential for the occurrence of the oxynitration reaction. If oxides of nitrogen are destroyed or prevented from forming by the addition of urea, the benzene is simply converted to phenylmercuric nitrate and polymercurated derivatives of benzene. On the other hand, a concentration of nitrogen oxides approaching saturation is very unfavorable and leads to poor yields of nitrophenols and the formation of dark colored by-products. The nitrogen oxide level equivalent to the presence of 0.05 *M* nitrous acid in 50% acid is estimated to be approximately the optimal concentration for the oxynitration reaction. Because of the experimental difficulties, little effort has been made to control this variable; it would appear to be a promising point for further investigation.

The use of aluminum nitrate in the low concentrations recommended by the Canadian investigators does not appear to have any influence on the oxynitration process.

Manganous nitrate, recommended by the Canadian investigators as a catalyst for the oxynitration and also for the destructive oxidation of oxalic acid, has

little effect in low concentrations. In concentrations of 0.5 M or higher it has a definite catalytic action on the rate of formation of DNP and the oxidation of oxalic acid; unfortunately, it also seems to catalyze the formation of nitrobenzene and the nitration of DNP to PA.

Preparatory Procedures

Four laboratory procedures, two batch and two continuous, have been developed for the oxynitration. In the first batch process[91] one liter of solution is used for the oxynitration of approximately 70 g of benzene. The solution is originally 10.65 M in nitric acid and 0.37 M in mercuric nitrate. Approximately 120 ml of 98% nitric acid is used to fortify the solution. The reaction time is 6 hours at 50 C. The benzene balance for such a run is as follows:

Benzene as dinitrophenol	68.4%	72.4%
Benzene as picric acid	4.0%	
Benzene as nitrobenzene	7.8%	
Benzene as *o*-dinitrobenzene	1.0%	
Benzene as *p*-dinitrobenzene	0.7%	
Benzene as 2,4,2′,4′-tetranitrodiphenylamine	0.5%	
Benzene as carbon dioxide	9.7%	
Benzene as oxalic acid	2.5%	
Benzene not accounted for	5.4%	

These yields were based on the benzene which remained in the reaction flask. In a typical run about 7.5% of the benzene introduced was lost by volatilization. This loss can be reduced by more efficient cooling and by absorbing the volatilized benzene in oxynitrating solution. The oxynitration solution after this reaction can be fortified to its original strength and used for a second run; this fortification and reuse can be repeated several times if appropriate methods are used to separate the picric acid and dinitrophenol from the neutral by-products which accumulate.

The second batch process—the batch extraction process—differs from the one just described in that, at the end of the 6-hour reaction period, a large excess of benzene is introduced with vigorous stirring. After the added benzene has dissolved the reaction products, the benzene solution is withdrawn and the aqueous solution is used to oxynitrate a fresh charge of benzene. On the assumption that a constant (predetermined) weight of benzene remains in the reaction after each extraction, it is possible to determine the yields; they are thus found to be comparable with those in the simple batch procedure described above. The process cannot be operated indefinitely without adding manganous nitrate to catalyze the oxidation of oxalic acid, which otherwise accumulates and precipitates as mercuric oxalate. When manganous nitrate is added it causes a slight increase in the production of nitrobenzene at the expense of the nitrophenols and increases the ratio of picric acid to dinitrophenol. In a typical run with 10.65 M nitric acid, 0.37 M mercuric nitrate, and 0.56 M manganous nitrate, the yields were 54.2% of dinitrophenol, 13.9% of picric acid, and 10.7% of nitrobenzene.

The first continuous process, known as the continuous solution process, operates on the following cycle. The oxynitration solution is saturated with benzene by vigorous agitation with excess benzene at room temperature; the saturated solution is separated from excess benzene and circulated through a heated coil; it is then cooled to room temperature and agitated again with benzene, which extracts the organic products and resaturates the oxynitration solution. In evaluating this process, the rate of formation of dinitrophenol per liter of reacting solution in the coil is determined; 70 g of dinitrophenol per liter per hour is representative performance.

The second continuous process, the continuous extraction process, involves the use of a continuous liquid-liquid extractor and an excess of benzene to remove the reaction products.[92] In steady-state operation this process will produce nitrophenols at a rate equivalent to 31 g of dinitrophenol per liter of oxynitration solution per hour. The yields of dinitrophenol, picric acid, and nitrobenzene are 44.1%, 29.2%, and 6.5%, respectively. Higher rates of oxynitration are possible, but the concentration of manganous nitrate necessary to bring about oxidation of the oxalic acid formed favors both the formation of nitrobenzene at the expense of nitrophenols and the formation of picric acid from dinitrophenol.

The most successful apparatus consists of a vertical cylindrical reactor equipped with funnels, condenser, outlet at bottom, and a side-arm near the top through which excess benzene containing dissolved reaction products can overflow into a separate receiver. The benzene is introduced into the bottom of the reaction mixture through a cluster of 22 capillary glass jets as a shower of small droplets which rise through the solution. The circulation rate is approximately 200 to 400 ml per hour; the effective reaction volume is 1,350 ml. No stirring of the solution is used other than that resulting from the movement of benzene droplets, convection currents, and fortifying acid. This is an important feature of the process, since the degree of dispersion of the benzene throughout the solution determines the rate at which benzene dissolves, and this in turn determines not only the rate of oxynitration

but also the proportions of products and by-products. Fortification with 98% nitric acid is continuous through a device which dilutes and disperses the strong acid before it can come directly into contact with liquid benzene. The reaction temperature is regulated by means of an external water jacket.

The benzene droplets rising through the solution partially dissolve and react while the remaining droplets extract reaction products and merge in a layer on the top of the acid solution. From the reactor this excess benzene overflows into a separate flask known as an "evaporator," which is heated in an oil bath to distil benzene and nitrogen oxides away from the reaction products into a second flask called the "boiler." The boiler is also heated to redistil the benzene through a condenser back again to the jets through which it is reintroduced into the oxynitration solution. The "evaporator" flask can be replaced without interrupting the operation of the reactor.

Reaction Mechanisms

The mechanism of the oxynitration reaction has been shown to be the following:[93]

$$C_6H_6 + Hg(NO_3)_2 \longrightarrow C_6H_5HgNO_3 + HNO_3 \quad (4)$$

$$C_6H_5HgNO_3 + N_2O_4 \longrightarrow C_6H_5NO + Hg(NO_3)_2 \quad (5)$$

The nitrosobenzene formed in reaction (5) is converted to mononitrophenol by two different paths. The first, reactions (6), (7), and (8), goes through a diazonium salt.

$$C_6H_5NO + 2NO \longrightarrow C_6H_5N_2NO_3 \quad (6)$$

$$C_6H_5N_2NO_3 + H_2O \longrightarrow C_6H_5OH + N_2 + HNO_3 \quad (7)$$

$$C_6H_5OH + HNO_3 \xrightarrow{NO_2} O_2NC_6H_4OH + H_2O \quad (8)$$

The second, reaction (6), involves oxidation and rearrangement.

$$C_6H_5NO \xrightarrow[\text{oxidation and rearrangement}]{HNO_3} O_2NC_6H_4OH \quad (9)$$

The nitrophenol, formed either in reaction (8) or reaction (9), is then nitrated further.

$$O_2NC_6H_4OH + HNO_3 \xrightarrow{NO_2} (O_2N)_2C_6H_3OH + H_2O \quad (10)$$

$$(O_2N)_2C_6H_3OH + HNO_3 \xrightarrow{NO_2} (O_2N)_3C_6H_2OH + H_2O \quad (11)$$

In solutions where the nitrite concentration is high and the nitric acid concentration is low, reactions (6), (7), and (8) take place; in solutions where the nitrite concentration is low and the nitric acid concentration is high, the oxynitration goes by way of reaction (9). The particular oxides of nitrogen specified in these reactions may be in error; frequently the reactions can be balanced on the assumption that more than one oxide of nitrogen is the active reagent or catalyst.

The experimental evidence for this mechanism is as follows. In the presence of urea, the concentration of nitrite in nitric acid is kept low. Under these conditions, a solution of mercuric nitrate in nitric acid converts benzene to the equilibrium mixture (4) containing phenylmercuric ion. This ion was identified by precipitation as phenylmercuric chloride. The equilibrium between benzene, mercuric nitrate, phenylmercuric nitrate, and nitric acid was approached from both sides, and the same value of the equilibrium constant obtained. Finally, the rate of mercuration of benzene by mercuric nitrate in the presence of urea was measured in nitric acid of varying concentration; the rate of the mercuration reaction was closely the same as the rate of the overall production of dinitrophenol in the oxynitration.[90a]

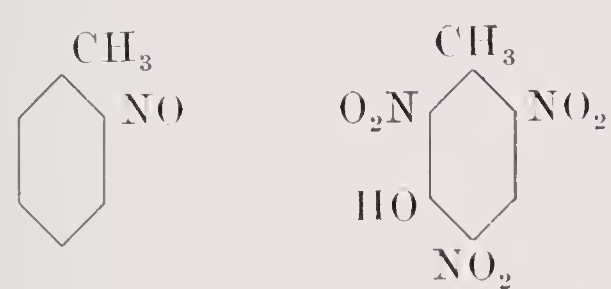
In the absence of urea or, more accurately, in the presence of nitrite, phenylmercuric nitrate reacts to form nitrosobenzene [equation (5)]. Part of the evidence for this step in the mechanism was supplied by the isolation of nitrosobenzene from the reaction mixture of phenylmercuric nitrate and nitrite in nitric acid solution.[90b]

In dilute nitric acid, nitrosobenzene further reacts with nitrite to form phenyldiazonium nitrate [equation (6)]. The diazonium salt could likewise be prepared by the action of nitrite on phenylmercuric nitrate [equations (5) and (6)]. This was demonstrated by isolating *p*-dimethylaminoazobenzene, a coupling product of the diazonium salt with dimethylaniline, in 78% yield. The rate of formation of the diazonium salt in dilute nitric acid solution was measured starting both from phenylmercuric nitrate and from nitrosobenzene. The rate of reaction from the latter compound followed a simple first-order reaction curve; whereas the rate of reaction, starting from the former, showed an induction period which could unambiguously be correlated with a two-step reaction, where both steps had approximately the same rate. The identification was definite because the rate of the second step [the conversion of nitrosobenzene to the diazonium salt, equation (6)] was independently determined.

In more concentrated nitric acid solution it was no longer possible to isolate a good yield of diazonium salt. The oxynitration nevertheless proceeded smoothly and gave better overall yields than in more dilute

[redacted]

solution. Since identical yields of diazonium salt were always obtained from phenylmercuric nitrate and from nitrosobenzene under all experimental conditions, it is very probable that nitrosobenzene is formed from phenylmercuric nitrate even in concentrated nitric acid solution. On the other hand, in concentrated nitric acid the yield of 2,4-dinitrophenol from phenylmercuric nitrate is greater than from phenyldiazonium nitrate, so the latter cannot be an intermediate under these conditions. A rearrangement of nitrosobenzene analogous to that of phenylhydroxylamine to *p*-aminophenol appeared possible. This rearrangement would be accompanied by or followed by an oxidation. That such a rearrangement actually occurs was made very probable by studying the reactions of *o*-nitrosotoluene. In dilute nitric acid in the presence of nitrite and mercuric nitrate, this compound forms a diazonium salt and is finally converted to 4,6-dinitro-*o*-cresol, in conformity with the predictions of the diazonium salt mechanism [equations (6), (7), (8)]. But in more concentrated nitric acid solution, no diazonium salt is formed, and *o*-nitrosotoluene is converted in excellent yield to 2,4,6-trinitro-*m*-cresol. In this reaction, it is apparent that the hydroxyl group has taken up a position para (or possibly ortho) to the original nitroso group.



The subsequent nitration of the partially nitrated phenols takes place at rates consistent with the assumption that they are intermediates in the reaction. The presence of certain by-products[90c] has likewise been explained, and is consistent with the mechanism advanced.

A related study[94] dealt with the mechanism of nitrite catalyzed nitrations of phenol and the nitrophenols. To this end, the equilibrium among HNO_2, NO_2, N_2O_4, NO, and N_2O_3 was studied in solution by means of a crude spectrophotometer (Coleman). N_2O_3 absorbs heavily in the region around 6,000 to 7,000 A and around 4,000 A, whereas NO_2 absorbs only in the region around 4,000 to 5,000 A. The two oxides of nitrogen can therefore be distinguished, and it is possible to analyze for each in the presence of the other. The ways in which the concentrations of these compounds vary with change in the concentration of gross nitrite (nitrous acid by titration) and with the concentration of nitric acid were determined. It was found that the concentration of N_2O_3 varied roughly as the square, the concentration of NO_2 with the square root, of the gross nitrite concentration. With increase in the concentration of nitric acid at constant gross nitrite concentration, the amount of NO_2 increases sharply; the amount of N_2O_3 is less affected.

Next the rate of nitration of phenol and of the nitrophenols was determined. Roughly speaking, the rate of nitration of *p*-nitrophenol increases 70-fold as the nitric acid concentration is increased from 10 to 60%; there are similar increases for the other phenols studied. The rate of nitration varies roughly as the square root of the gross nitrite concentration. The effect of change in nitrous and nitric acid concentrations on the rate of nitration parallels the affect of these changes on the concentration of NO_2, and it therefore becomes probable that NO_2 is the active catalyst in the nitration of phenols. It was also noted that the nitration of anisole, catalyzed by oxides of nitrogen, resulted in the loss of the methyl group to give dinitrophenol as the product. On the basis of these facts, a tentative mechanism for the nitration of phenols was advanced.

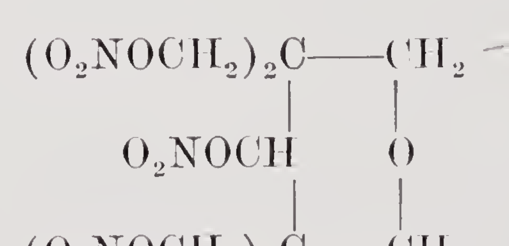
No explanation was advanced for the considerable decomposition which accompanies the mononitration of phenol.

1.7 NITRATE ESTERS

Work in this field has been confined to a very few substances;[f] and, with one exception, has dealt with the preparation of the alcohols to be nitrated rather than with the preparation of the nitrate esters themselves.

A survey of the literature showed neither natural sources nor preparative methods which could be developed in any reasonable time to furnish significant amounts of erythritol or its stereoisomers.[96] No experimental work was done.

The preparation of anhydroenneaheptitol was investigated as the first step in a study of its pentanitrate (I).



I

[f]Twelve sugar alcohols and glycosides were prepared for the determination of their heats of combustion and their behavior on nitration, but no further work was done with them.[95]

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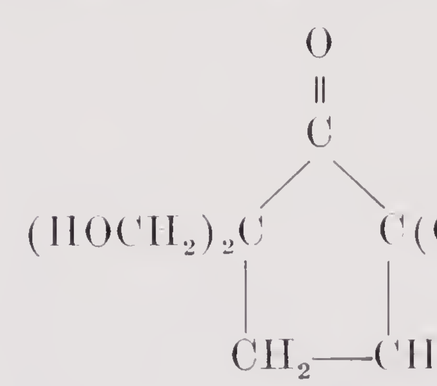
A procedure was developed which permitted the preparation of anhydroenneaheptitol in 50 to 57% yield from formaldehyde and acetone. The reaction must be run at high dilution, which makes it necessary to evaporate a large volume of water in order to isolate the product. Further, only about one-half of the product can be isolated as such; the remainder is obtained by converting the material to its dibenzylidene derivative and then hydrolyzing this derivative.[97] No further work was done with anhydroenneaheptitol, but the material obtained in the preparative study was nitrated and the explosive properties of the nitrate were determined. Anhydroenneaheptitol pentanitrate has an impact sensitivity comparable with that of RDX; its power in the ballistic mortar is 137% of that of TNT, or about midway between tetryl and RDX.[98]

A study of the preparation of pentaerythritol, PE, from formaldehyde and acetaldehyde showed that the yield of crude PE is about 10% greater when the aldehydes are added to an aqueous suspension of calcium hydroxide, than when lime is added to the aldehydes. The preferred procedure furnishes a 66 to 68% yield of crude PE; this product assays about 86% PE, so that the yield of pure PE is about 58%. A number of promoters, which have been recommended for the reaction, were tried and found to be of no value. A bibliography and description of the methods of preparation of PE reported in the literature are included in the report of the work.[99]

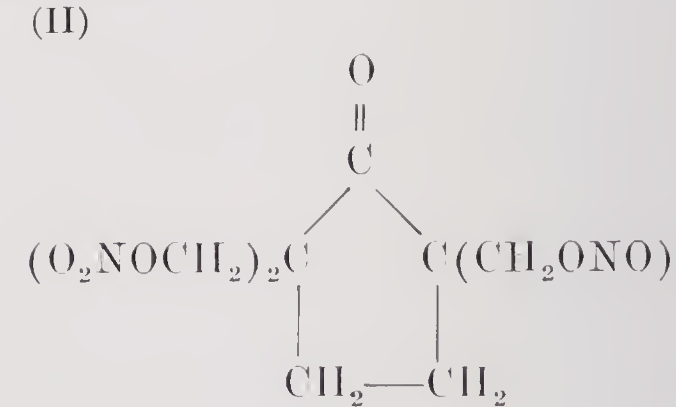
A later study of the same reaction confirmed the observation that addition of the aldehydes to the lime gave better yields of PE than did addition of lime to the aldehydes; however, the latter order of addition gave a PE of better quality. Acetaldehyde can be replaced by crotonaldehyde without lowering the quality of the PE, but with a loss in yield; acetaldehyde can be replaced by aldol without lowering either the quality or the yield. Aldol is more convenient to use than acetaldehyde. Only slight differences in yield and quality of PE resulted when paraformaldehyde was substituted for formalin. Paraformaldehyde absorbs heat on depolymerization and this makes the control of temperature easier. By adding lime to the mixture of aldehydes, a 60 to 67% yield of PE which is 92 to 93% pure is obtained; by adding the aldehydes to the lime a 65 to 68% yield of PE which is 87 to 88% pure is obtained. The importance of the second exothermic reaction, presumably the destruction of the excess formaldehyde, is stressed. A detailed procedure for the assay of crude PE by means of its benzylidene derivative is described.[100]

The single nitrate ester whose preparation has been studied in detail is Fivonite [2,2,5,5-tetramethylolcyclopentanone tetranitrate (III)], a substance described in the chemical journals and in patents before the war.[101-103] The interest of Division 8 in this material was twofold: as a high explosive which might replace TNT in mixed explosives analogous to Composition B, Ednatol, and Pentolite, and as a substitute for nitroglycerin in double-base powders.

Fivonite is a solid melting at 68 C; it possesses satisfactory stability; its impact sensitivity is between those of RDX and tetryl; its power is comparable with that of tetryl; and the starting material for its synthesis is not in demand for the preparation of either TNT or synthetic rubber. Tests on mixtures of Fivonite with RDX, Haleite, and PETN showed that these mixtures were more powerful and more brisant than the corresponding mixtures made with TNT, but this improved performance was offset by increased sensitiveness.[104] The use of Fivonite in place of nitroglycerine as a plasticizer for nitrocellulose in double-base powder proved successful, but a competitive material, DINA, proved to be more satisfactory than Fivonite (see Section 6.7, Albanite Powders). As a result, Fivonite was not used. The synthetic procedures described in the following paragraphs, however, make it available if a demand should arise.



(II)



(III)

Fivonite is prepared from cyclopentanone by means of two reactions.

1. Purified cyclopentanone is mixed with formaldehyde, as 37% formalin, in the ratio of 1 mole to 4.2 moles. Sufficient freshly prepared calcium hydroxide is added to bring the *p*H of the reaction mixture to 9, and additional calcium hydroxide is added as necessary to keep the *p*H at this value. The reaction,

which is exothermic, is complete in two hours. The base is neutralized with hydrochloric acid and the product, Fivone, 2,2,5,5-tetramethylolcyclopentanone (II), is isolated in 90 to 95% yield by vacuum drying on the steam bath. This product is suitable for the nitration.

2. Fivone, powdered to pass a 4 to 6 mesh screen, is added portionwise to six weights of 98% nitric acid, stirred and cooled to 10 C. The reaction is mildly exothermic. After 30 minutes the reaction is drowned in about 4 weights of chipped ice with stirring. The product, Fivonite, is stabilized by stirring under hot water, adding sodium carbonate to neutralize the acid, cooling, and decanting the water from the solidified Fivonite. The yield of once-stabilized product is 95%. The procedure furnishes 4.3 pounds of once-stabilized Fivonite per pound of cyclopentanone.[105]

The synthetic work described above was done with cyclopentanone prepared from adipic acid. In order to make Fivonite available in quantity, a synthesis from petroleum cracking fractions was developed.[106] This synthesis involves the following steps:

1. Dehydrogenation of cyclopentane to cyclopentadiene.

2. Hydrogenation of cyclopentadiene to cyclopentene.

3. Hydration of cyclopentene to cyclopentanol.

4. Dehydrogenation of cyclopentanol to cyclopentanone.

5. Condensation of cyclopentanone and formaldehyde to Fivone.

The overall yield of Fivone is 57% based on cyclopentane, and plans are available for a pilot plant capable of producing 23,000 pounds of Fivone per day.

In order to duplicate a German rocket powder, some 500 pounds of diethylene glycol dinitrate (DEGN) were prepared from diethylene glycol. No difficulty was experienced in nitrating the glycol in 8.6-pound lots with a nitric acid ratio of 1.85 at a temperature of 50 F. The yield of washed neutralized DEGN was 75%. On the basis of this work there seems to be no reason why the large-scale manufacture of DEGN should not be technically feasible.[107]

1.8 EXPLOSIVE AND COMBUSTIBLE POLYMERS[s]

In some of the early projects undertaken by Division 8, several problems arose which appeared to call for binders of polymeric materials. Typical uses for such materials would be as binders in tracer and igniter compositions and composite propellants and as substitutes for charcoal in time-ring fuzes. For such uses it would be desirable to have a series of binders containing varying amounts of oxygen in the binder molecules. In this way binders could be chosen which would not seriously disturb the oxygen balance of the systems in which they were used. Such materials were not available, since the synthesis of polymers of such structures had not been studied. It, therefore, seemed worth while to sponsor scouting work in this field. A brief study was made at the University of Illinois and a much more comprehensive one by the Rohm & Haas Company. Research was terminated when a wide variety of polymers had been prepared with a considerable variation in physical properties. At that time, it seemed advisable to make these materials available for studies in mixtures before going further with the preparative research. Unfortunately, urgent projects have prevented the full evaluation of these materials as binders in explosive and propellant compositions.

In addition to the general work mentioned above, a specific request was received for a study of the nitroindene polymer (NIP) developed in Great Britain. Samples of this material were prepared at the University of Pennsylvania and submitted to Picatinny Arsenal for tests as a substitute for charcoal in time-ring fuzes. NIP proved to have interesting properties, but its development has not progressed to the stage of service applications.

The polymeric materials for binders were prepared in three general ways.

1. The reaction between a molecule containing nitro groups and a polymer. See (a) and (c), below.

2. The nitration of polymeric materials. See (b) and (h), below.

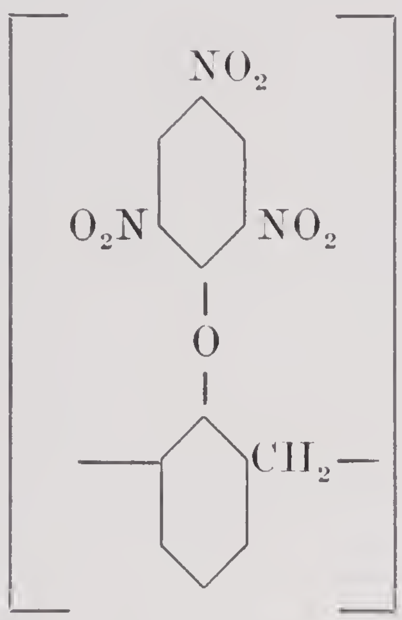
3. The polymerization of materials containing nitro groups. The materials to be polymerized were usually obtained by combining a molecule containing nitro groups with a second molecule which is capable of undergoing polymerization. See (d), (e), (f), and (g), below.

By these procedures, polymers[76,77,108-110] of the following types were prepared.

a. Picryl and dinitrophenyl ethers obtained by the reaction between picryl chloride or 2,4-dinitrochlorobenzene with phenol-formaldehyde resins. Products were prepared from phenol, cresol, and *p*-tert-butyl-

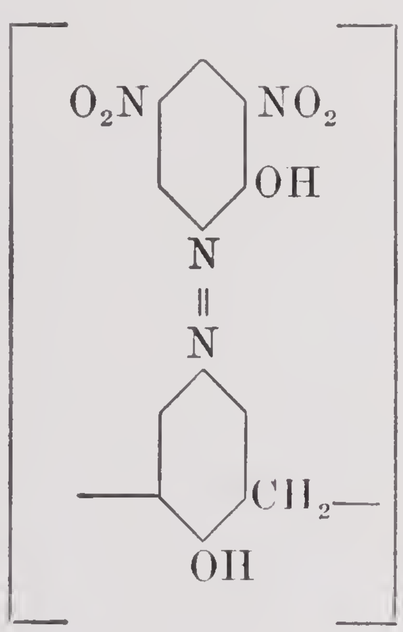
[s]This section is constructed from a summary prepared by Ralph Connor.

phenol. A typical structural unit in one of these polymers is shown in the formula below.



b. Nitration products of the above ethers and of the polybenzyls.

c. Azo resins obtained by coupling the diazonium salts from picramic acid or 2,4-dinitroaniline with various phenol-formaldehyde resins and with abietic acid.



d. Polymerized nitrostyrenes. These products were obtained from ω-nitrostyrene, *m*-nitro-ω-nitrostyrene, 1-nitro-2-furylethylene, and by the condensation of 2,4,6-trinitrobenzaldehyde with nitromethane, and the condensation of trinitro-*m*-xylene with formaldehyde.

e. Polymerizable esters of trinitrophenylethanol. When TNT is allowed to react with formaldehyde under appropriate conditions, a high yield of 2,4,6-trinitrophenylethanol is obtained. This alcohol was esterified with acrylic and other unsaturated acids. The resulting esters are readily polymerized.

f. Nitroalkyl esters. Nitro alcohols may be obtained by the reaction of nitroparaffins with aldehydes. These nitro alcohols were converted to acrylate esters and to esters of other unsaturated acids. The esters polymerize readily.

g. Products from the reactions of TNT or DNT with formaldehyde and amines. These reactions gave resinous products when TNT was used with primary amines or ammonia. When secondary amines were used with either TNT or DNT the products were not polymers but were crystalline β-dialkylaminoethyl derivatives of trinitrobenzene.

h. Miscellaneous resins. These included resins obtained by the reaction of nitromethane and formaldehyde with aniline and nitroaniline. Resins obtained by the reaction of formaldehyde with fluorene or with phenol and aniline were nitrated.

Stability and impact sensitivity tests were carried out on a considerable number of the products. It may be concluded from the information at hand that it is possible to prepare polymers which are readily combustible and which have melting points ranging from room temperature to well above 200 C. Products may be obtained which have satisfactory stability and sensitivity.

A few attempts were made to use these resins in casting compositions containing a high percentage of solids and to use nitro esters as plasticizers in solventless double-base powders.[111] Neither of these experiments showed great promise, but the experiments were by no means exhaustive.

1.9 MISCELLANEOUS HIGH EXPLOSIVES[t]

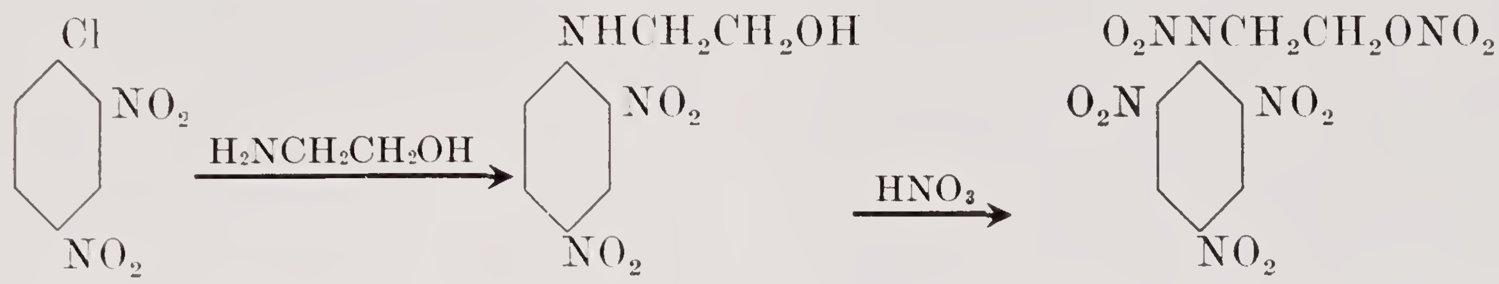
In this section are included a variety of candidate high explosives and intermediates which do not fall into any of the categories considered in the preceding sections.

1.9.1 Analogs of Tetryl Containing Nitrate Ester Groups[112-114]

A number of aminoalcohols have become available or potentially available in recent years. Condensation of these aminoalcohols with dinitrochlorobenzene followed by nitration furnishes explosives analogous to tetryl, but containing, in addition to C-nitro and N-nitro groups, one or more nitrate ester groups. The general scheme of synthesis is illustrated with dinitrochlorobenzene and ethanolamine.[u]

[t]This section is constructed from information furnished by S. R. Aspinall.

[u]Attempts to prepare some of the intermediates by the reaction between aniline or the nitranilines and glycerine monochlorohydrine or epichlorohydrine did not give satisfactory results.



The condensation may be effected by adding the aminoalcohol to an alcoholic solution of dinitrochlorobenzene and then adding one equivalent of aqueous alkali. Alternatively, the two organic reactants may be mixed, then fused, and the melt, after cooling, purified by crystallization. Purification of the dinitrochlorobenzene by sweating improves both the yield and the quality of the condensation products. The structure of the aminoalcohol affects the yield in the condensation and dictates the choice of experimental conditions to be used in the condensation. The nitration, the second step in the synthesis, can be done with mixed acid, but dilute nitric acid alone gives purer products in better yields.

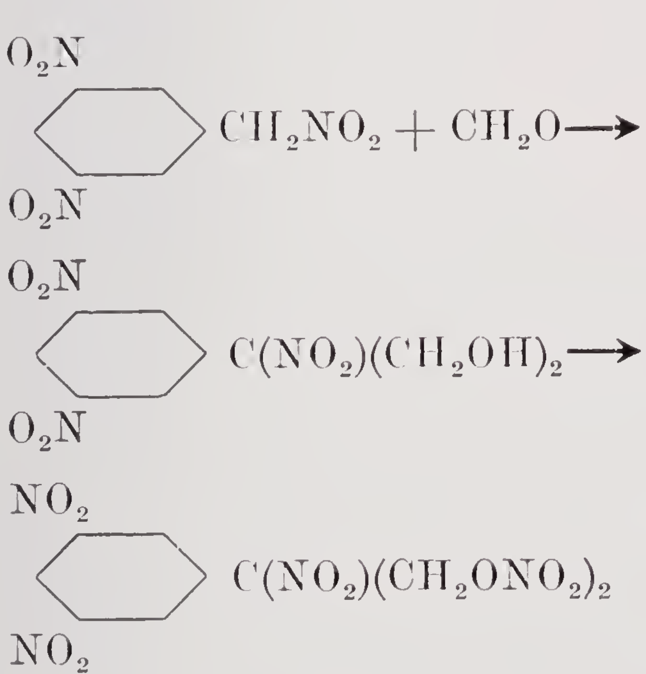
Two of the products obtained in the work—Heptryl (I) and trinitrophenylisobutylolnitramine nitrate (II)—showed promise but were found to offer no advantages over explosives already in use.

$$(O_2N)_3C_6H_2N(NO_2)C(CH_2ONO_2)_3$$
(I)

$$(O_2N)_3C_6H_2N(NO_2)C(CH_3)_2CH_2ONO_2$$
(II)

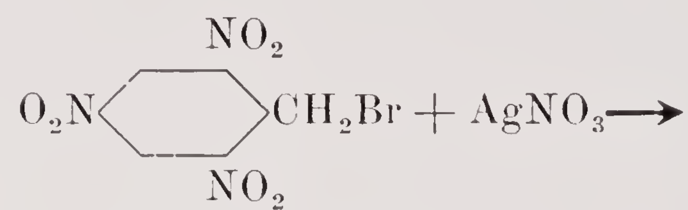
1.9.2 Aliphatic-Aromatic Nitro Compounds and Nitrate Esters[115]

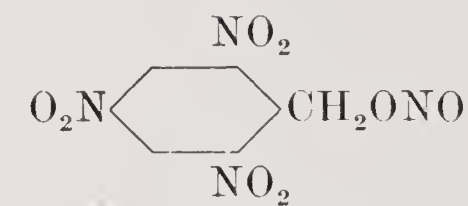
Two products (III) and (IV), whose power in the ballistic mortar is equal to that of tetryl, have been prepared. The first of these was obtained by condensing 3,5-dinitrophenylnitromethane with formaldehyde and nitrating the condensation product.



(III)

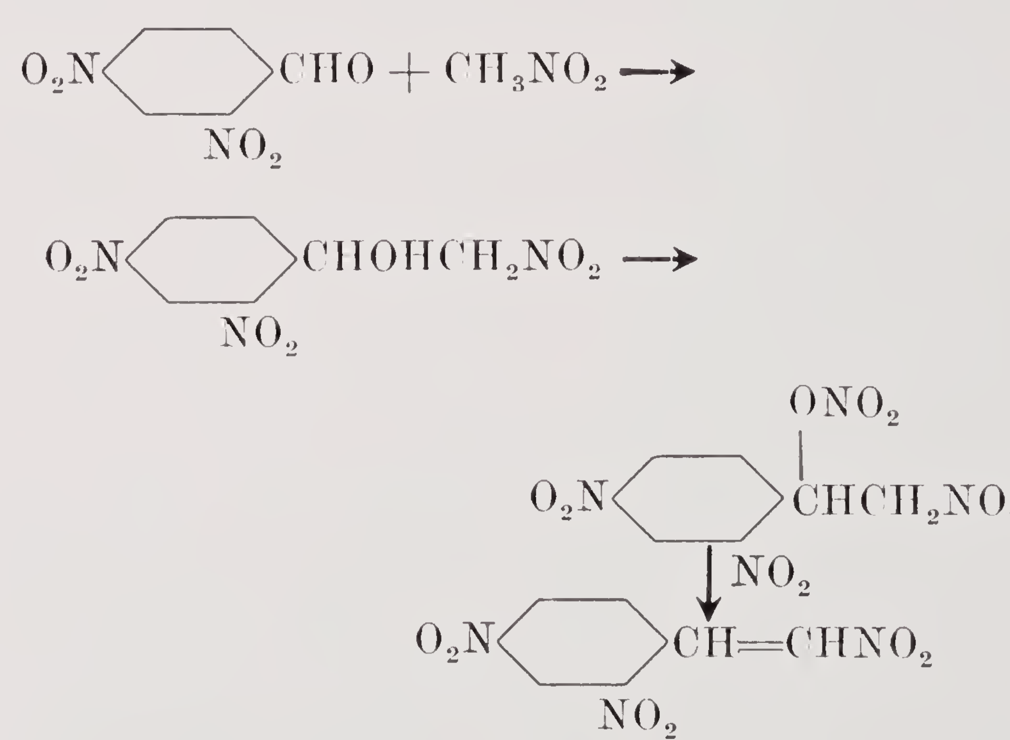
The second was prepared from trinitrobenzyl bromide, either by treatment with silver nitrate or by hydrolysis to the alcohol and subsequent esterification.





(IV)

In the same investigation the condensation of 2-nitrobenzaldehyde and 2,4-dinitrobenzaldehyde with nitromethane was shown to lead to stable nitroalcohols. The nitrates of these alcohols, however, lose nitric acid readily on warming in solution and furnish nitrostyrenes.



2,4,6-Trinitrobenzaldehyde does not condense with nitromethane.

Also in the same investigation a study was made of the Ponzio reaction—the conversion of benzaldoxime to phenyldinitromethane by means of nitrogen dioxide. It was shown that the reaction is best run by adding benzaldoxime to an ether solution of nitrogen dioxide. Attempts to extend the Ponzio reaction to *o*- and *p*-nitrobenzaldoxime, to *o,p*-dinitrobenzaldoxime, and to 3-nitro-4-methoxybenzaldoxime were not successful.

1.9.3

Nitrofurans[116]

The study of the nitration of furans was undertaken because a number of furan derivatives are available in large quantities, because 2,5-dinitrofuran has been reported to be comparable with TNT as a high explosive, and because no satisfactory procedure is known for the preparation of dinitrofuran or any other polynitrofuran. The study showed that, while it was usually possible to introduce a nitro group in the 5-position of a furan derivative appropriately substituted in the 2-position, it was not possible either to nitrate in the 3- and 4-position, or to introduce more than one nitro group. Since no furan derivatives sufficiently highly nitrated to be of interest as explosives were obtained, a list of those nitrofurans which were prepared and those which could not be prepared is not given here. This information is available in the original report.

The reasons which prompted the study of the nitration of furans are still valid. As a result of the study which has been made, however, it is clear that the status of this problem is the same as that of the nitroparaffins discussed in Section 1.6; a considerable increase in our knowledge of the chemistry of furans will be necessary before we can hope to prepare nitrofurans which will be of interest as explosives.

1.9.4

Trinitro-*m*-xylene[117]

Trinitro-*meta*-xylene has received a certain amount of attention as an explosive and for this reason it appeared desirable to investigate the possibility of increasing the supply of *meta*-xylene should a large demand for the material suddenly arise.

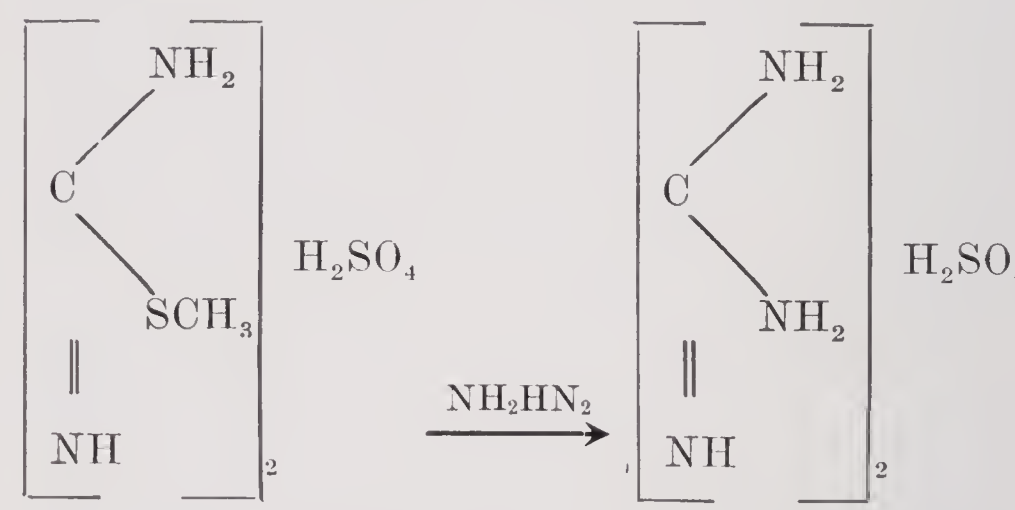
Commercial xylene is a mixture of *ortho, para,* and *meta* isomers, only the last of which can be converted readily to a stable trinitro derivative. It has been found that heating commercial liquid xylene with anhydrous aluminum chloride does not result in an increase in the percentage of the *meta* isomer at the expense of the other two. This is consistent with the fact, previously reported and confirmed during this work, that each of the pure isomers when heated with aluminum chloride is converted to an equilibrium mixture of isomers which does not differ significantly in composition from commercial xylene.

Mixtures of commercial xylene and naphthalene were heated with aluminum chloride in the hope that the *ortho* and *para* isomers would methylate the naphthalene and leave a mixture of *meta*-xylene and toluene. However, very little toluene was formed and the *meta*-xylene content of the commercial xylene was unchanged.

1.9.5

Aminoguanidine[118]

The preparation of aminoguanidine was studied in order to make available this raw material for the synthesis of tetracene. The reduction of nitroguanidine with zinc and hydrochloric or acetic acids gave aminoguanidine of poor quality in poor yield; the product contained zinc, which was difficult to remove. The reaction between methyl isothiourea sulfate and hydrazine furnished aminoguanidine in quantitative yield. The reagents used in this reaction are so expensive, however, that the process is not practical.



Electrolytic reduction of nitroguanidine furnished aminoguanidine in 75% yield. The reduction is carried out in a 5% solution of sulfuric acid, using amalgamated lead cathodes, with a current density of 1 amp per square decimeter; the current efficiency is 38%. The bulk of the aminoguanidine is isolated as the acid sulfate, the remainder as the bicarbonate. Electrolytic reduction should be suitable for the commercial preparation of aminoguanidine at an estimated cost of 50 cents to $1.00 per pound.

1.9.6

Other Candidate High Explosives

Preparatory procedures have been worked out for the *bis*-trinitrophenyl ether of ethylene glycol, for β-(2,4,6-trinitrophenoxy)ethyl nitrate, for hexanitrodiphenylethylenedinitramine (ditetryl), and for trinitrophenylguanidine. Attempts to synthesize nitrated hydroxyethylguanidines were not successful. No practical synthesis of hexanitroazobenzene could be developed. Some nitrated phenylbenzotriazoles were prepared, but they were not attractive as high explosives.

1.10

PLASTIC HIGH EXPLOSIVES[v]

By 1941 the British had developed and put into use the plastic high explosive PE-1. This material,

[v]This section is taken from reports[119] by E. H. Eyster.

which has the consistency of a good modeling clay, contains 88.3% RDX plasticized and desensitized by 11.7% of a special PE oil. Its plasticity permits it to be molded by hand and its stickiness ensures intimate contact with the target, so that full advantage may be taken of its high brisance. It is particularly suited for the attack of rails, girders, and other steel targets of irregular outline, since it may be shaped in the field. At the same time, the plasticizing oil greatly desensitizes the material, so that it is relatively safe to handle and carry even under fire. Such a material is clearly an ideal agent for light demolition and sabotage. Indeed, the British production of PE-1 and its successor, PE-2 were almost completely allocated to special service forces and to underground forces within enemy-occupied countries. For such use the finest plastic properties were demanded, but great tonnages were not required. These circumstances have naturally determined the British acceptance standards for plastic explosives; since all our original information concerning plastic explosives was derived from British sources, our ideas of what constituted an acceptable plastic explosive, were also thus determined.

In October 1941, attempts to prepare British PE-1 were begun at the Explosives Research Laboratory. The PE-1 oil is prepared by heating 10% of crepe rubber in a 2/1 vaseline-paraffin oil base at 150 C for about 15 to 16 hours with vigorous stirring. The plastic is prepared from this oil and RDX of which 50 to 70% should be through 30 and retained on 200 USS *Sieve*, and 30 to 50% should be through a 200 USS *Sieve*. Twelve parts of molten PE oil are added to 88 parts of RDX as a 5/1 (water-RDX) slurry in hot water. After about 5 to 10 minutes' stirring, the RDX is well coated with oil; excess water is then filtered off, the wet product is roll-milled and finally dried.[120] Experimental work with PE-1 continued until May 1942 and consisted in the main of attempts to prepare suitable PE-1 oils, studies of proper milling and drying conditions; and, finally, the preparation of a motion picture showing the preparation of PE-1 and typical uses of the plastic explosive, intended to stimulate interest in plastic explosives among the Services.

By this time the British were at work on a new plastic which would avoid the use of rubber, both because it was becoming short in supply and also because PE-1 deteriorated on aging, particularly in the presence of air and light. The period of study of PE-1 at the Explosives Research Laboratory served therefore mainly as an introduction to the art of preparing good plastics. During this period it was established that the particular difficulty with PE-1 (and, it appears, with most similar plastics) is to get the material through the drying stage without notable deterioration in plastic properties; only if the milling technique is correct can this be achieved. No PE-1 sample was made in which the behavior during drying could be considered ideal; but changes in the springing of the rolls (the rolls were originally held rigidly at a predetermined separation) made it possible to obtain fair products, whereas the early batches dried to hopelessly crumbly materials. It was found, however, that excellent PE-1 samples could be made by a dry process, the molten oil being mixed with dry RDX and the milling being carried out dry. This dry process was later used for rapid tests of substitute PE oils, on the assumption that unless an oil could produce a good plastic under these circumstances it could not produce a good plastic by the wet process.

In May 1942 work began on development of substitutes for the PE-1 oil. First, substitutes for the rubber only were studied, no attempt being made to modify the 2/1 vaseline-paraffin oil base; but later other oils were studied, either alone or with the addition of vaseline, wax, or materials like lecithin, lanoline, Alox, believed to act as surface agents. By the end of 1942 the art of roll-milling was well developed, and a 66/34 vaseline-Voltolized rapeseed oil mixture had been produced as a substitute PE oil. At the same time, however, the British PE-2 oil, 110/55/10 vaseline-paraffin oil-lecithin, had been developed and a sample of this oil had been received. Plastics made with the two oils were carefully compared, and it was decided that the Voltolized rapeseed oil product was not clearly superior to the British PE-2. The latter material was then adopted for manufacture in this country as RDX Composition C.

It was then soon found that both British PE-1 and Composition C (British PE-2), and also the 66/34 vaseline-VRO plastics became very hard and difficult to mold at low temperatures, owing to their vaseline content. This finding led to the request that a plastic explosive be developed which could be molded at low temperatures. RDX Polar PE, based on a viscous high-viscosity lubricating oil plus lecithin, was developed to meet this request. This plastic has the composition 88/12 RDX-oil; the oil is a 95/5 mixture of Gulf 300 Process Oil and lecithin. At the same time the du Pont Company developed an RDX plastic plasticized with a mixture of nitrotoluenes thickened with nitrocellulose. This material remained workable

at low temperatures for a considerable period due to supercooling of the plasticizer, and excelled Composition C in low-temperature plasticity. It is not of high quality as a plastic and tended to deteriorate further in plastic properties during hot storage. It could, however, be turned out in far greater tonnages than Composition C or the RDX Polar PE and was somewhat more powerful. It was adopted as Composition C-2 and, together with a later variant, Composition C-3, has been the plastic explosive used by the U. S. Army Engineer Corps.

In May 1943 a request was issued for plastic explosives based on some other explosive than RDX, but which could be reliably fired by an Engineer Special Detonator. This last requirement eliminated explosives based on TNT, ammonium picrate, or tetryl. In August a PETN plastic, PEP-2 (85/15 PETN-Gulf Crown Oil E) had been developed.[121] It was modified, after a pilot-batch had been made at the Eastern Laboratory of the du Pont Company, to an 86/14 PETN-Oil composition and was then called PEP-3. During the preparation of a second pilot-batch it was found that this material collected static electricity and, during the extrusion process employed in the packaging operation, produced large sparks. Attempts to prevent this by increasing the conductivity of the oil were not successful. In the meantime, RDX production had so increased that need for such a material had passed. PEP-3 did, unexpectedly, prove superior to RDX plastics in one respect: it was much more difficult to set on fire.

In November 1943 a request was made for an explosive whose plastic properties might be rather poor, but whose sensitivity should be distinctly lower than that of Composition C-2. For this purpose two insensitive semiplastics were suggested, RIPE (85/15 RDX-Gulf Crown Oil E), and PIPE (81/19 PETN-Gulf Crown Oil E). It was intended that these materials would be used to load special shells and rocket heads for "plaster shot" attacks against reinforced concrete. About a year later, lots of each plastic were made at Picatinny Arsenal; only the RIPE proved satisfactory, but it had rather a low density and, although tested, has not been used in service.

1.11 EXPLOSIVE COMPOSITIONS[w]

A highly characteristic development of World War II was the use of such sensitive and powerful high explosives as RDX, desensitized by the addition of either a less sensitive, less powerful explosive, such as TNT, or a wax, or both. In this section is described the work done by Division 8 on the development of these explosive compositions. For completeness of coverage reference should also be made to the PT Interim Reports of Division 8.

1.11.1 Composition A[120,122-125]

This RDX composition, developed by the British in order to reduce the sensitivity of RDX sufficiently to permit its use as the main filling in projectiles, was composed of RDX and beeswax in the ratio 91/9. Beeswax is an excellent desensitizer, but it was not available in amounts adequate for the large production of densitized RDX envisaged in the United States. A search was therefore made for substitutes for beeswax. From the wide variety of waxes examined the conclusion was drawn that practically any petroleum-base wax becomes a possible substitute for beeswax if some polar additive, such as, for example, Alox 600, is added to the wax in amounts of from 1 to 10%. Such a modified wax will wet RDX from water in the same way as does beeswax, and almost any such wax seems to have about the same desensitizing action as beeswax. The most satisfactory substitutes for beeswax must therefore be chosen not on the basis of any special effectiveness as desensitizers but, rather, on the basis of availability, physical properties (such as consistency, melting point), and ability to withstand hot storage without exudation of oil or low-melting wax. A series of such substitute waxes was recommended for Composition A early in 1942. One of them, which has been called Bruceton Wax No. 10, was adopted and has been used both in Composition A and in Composition B (see below). Bruceton Wax No. 10 has the composition 90/10 Aristowax 160-165 (Union Oil Company of California)—Alox 600 (Alox Corporation, Niagara Falls, N. Y.). Subsequent studies showed that even more desirable substitute waxes are available for use in Composition A; a 99/1 Stanolind Wax 170-175, Alox 600 mixture seems particularly good from the standpoint of exudation.

1.11.2 Composition B[126-128]

The British Composition B was composed of RDX-TNT-beeswax in the proportion 60/40/1. Bruceton Wax No. 10 was found to be a satisfactory substitute for the beeswax in the composition. In Composition B, desensitization of the RDX is accomplished mainly by the TNT, although the wax makes a real, albeit

[w]This section is based on reports prepared by E. H. Eyster.

Table 1. Properties of plastic explosives.

	Composition C (British PE-2) (1)	ERL 66/34 vaseline-VRO PE (2)	ERL RDX Polar PE (3)	Du Pont composition C-2 (4)	ERL PEP-1 (5)	ERL PEP-2 (6)	Du Pont PETN gelatine SWV-9 (7)	ERL RIPE (8)	ERL PIPE (9)
1. Physical properties									
a. Density (25 C; g/cc)	1.60	1.61	1.60	1.57	1.48	1.47	1.50	1.36	1.31
b. Extensibility (25 C; mm)	11	22	~50	9	3	13	....	....	....
c. Compression plastometer constants:	*a* *b*	*a* *b*	*a* *b*	*a* *b*	*a* *b*	*a* *b*	....	....	....
25 C	11 7	15 10	11.4 65	3.3 27	9.5 3.9	25 45			
0 C	~2 at 15 ~3 at 15	Hardens	7.0 14	3.3 7.6	.. ..	11 29			
— 20 C		about	4.1 5.5	3.3 4.6	3.3 11.0	.. ..			
— 35 C		like (1)	1.5 3.7	2.5 4.2	.. ..	2.6 3.9			
d. Sagging test (25 C; mm)	3	8	....	....	..	....	....	....	....
e. Stickiness [25 C; W_{10}(g)]	230	230	51	23	168	....	....	....	....
f. Remarks on plasticity	Excellent plastic at 25 C	Very extensible; softer than (1) in general	Softer than (2) at 25; in general	Fair plastic when fresh	Good plastic—generally shorter than (1)	Rather like (3), but usually less soft	Somewhat like (4), but more gelatinous	Semiplastic	Semiplastic
2. Explosive properties									
a. Bullet test (% inert)									
Cal. .30 ball, 1″ pn	100% (4 trials)	80% (5 trials)	100% (10 trials)	100% (10 trials)	100% (6 trials)	90% (20 trials)	50% (10 trials)		
Cal. .50 ball, 2x3″ pn	......	....	100% (1 trial)	40% (10 trials)	....	44% (9 trials)	....	100% (20 trials)	66% (19 trials)*
Cal. .30 ball, ½″ backed ½″ steel	......	....		100% (2 trials)		100% (2 trials)			
b. Flame sensitivity (II)	......	....	138	178	....	Will not break in test	50	162	....
c. Cap sensitivity: No. 6 fulm. chl.			3 NE (3 trials)	3 NE (3 trials)	5E (5 trials)	10 NE (10 trials)	5 NE (5 trials)	....	....
No. 8 Tetryl	10 E (10 trials)	10 E (10 trials)	25 E (25 trials)	23 E (25 trials)		10 E (10 trials)	5 E (5 trials)	....	....
d. Velocity of detonation (m/sec) (density)	8100 (1.590)	8100 (1.590)	8110 (1.581)	7800 (1.579)	....	7540 (1.42)	....	7320 (1.35)	6930 (1.31)
e. Ballistic mortar (TV)	125	125	125	142					
f. Brisance-plate denting test. (Cast TNT = 100)					108	115	....	118	~106
Method A; (density)	112 (1.581)	(112)	(112)	118 (1.572)	95 (1.488)	100 (1.487)	....	....	....
Method B; (density)	......	....	....	111 (1.52)	....	....	~110 (1.50)	85 (1.37)	76 (1.33)
3. Stability									
a. 135 Thermal stability	......	....	Not acid 300′	Not acid 300′	Acid 95′	Acid 160	....	....	....
b. Vacuum stability in 90′ (gas evolved-cc) in 48 hr	......	....	$\left.\begin{matrix}0.51\\7.7\end{matrix}\right\}$ 120 C	$\left.\begin{matrix}3.8\\>12\end{matrix}\right\}$ 120 C†	$\left.\begin{matrix}0.50\\3.22\end{matrix}\right\}$ 100 C	>12, 48 hr 120 C ~0.3, 48 hr 100 C	....	$\left.\begin{matrix}0.43\\0.54\end{matrix}\right\}$ 120 C	>12, 48hr 120 C 0.5, 48hr 100 C
c. Exudation, closed (% total wt lost at 50 C in 1 week)	0.8%	0.7%	0.3%	3.0%	....	1.2%	4.4%	25% (60 C)	6.1% (60 C)
d. Remarks on storage stability of plastic properties	Very good at elevated and ordinary temperatures if lecithin is good.	Very good retention at ordinary and elevated temp. Stored 3 years in perfect state	Same as (1) Samples have been stored 2½ yr at ord temp and are still perfect	Extensibility quickly deteriorates. Hardens in elevated temp storage	Hardens in storage, esp. at elevated temp	Very good. Samples stored 2 yr are in perfect state	Same as (4), or perhaps poorer	....	....

*Only with PIPE have high-order failures in the bullet test been obtained.

†This result is not very meaningful because of the volatility of the plasticizer in Composition C-2.

relatively small, contribution to the desensitization.

Composition B is used for the pour filling of projectiles. Consequently a great deal of time and effort have gone into the study of the factors determining the consistency and the flow properties of the material. The effects of temperature, concentration of RDX, grist of RDX, stirring, and surface-active agents have been studied in detail and are described in the reports already cited.

1.11.3 Miscellaneous Explosive Compositions

As part of the development of Haleite (see Section 1.3) mixtures of Haleite and TNT, known as Ednatols, have been prepared and studied for comparison with Pentolite and Composition B. It is possible to prepare Ednatols which are pourable and which are less sensitive than Composition B; these pourable Ednatols, however, are inferior to Composition B in stability, density, and performance. A surface-active agent, the acetone extract of soybean lecithin, has been found to improve the fluidity of Ednatols.[128,129]

Analogs of Cyclotol, Pentolite, and Ednatol have been prepared from RDX, PETN, and Haleite using Fivonite in place of TNT. Since Fivonite is more powerful than TNT, it was expected that these compositions would be more powerful than the corresponding ones made with TNT. This was found to be so, but the improvement in performance was accompanied by so marked an increase in sensitivity that the Fivonite compositions were not felt to be of any practical value.[104]

Brief studies, to be found in the PT Interim Reports, were made on the explosive properties and pouring properties of such compositions as PTX-1, PTX-2, 70/30 Cyclotol, and 52/48 Picrotol.

1.12 ALUMINIZED EXPLOSIVES[x]

The introduction of aluminized explosives for underwater and air blast use was, like the introduction of the explosive compositions treated in the preceding section, characteristic of World War II. In this section is presented the work done by Division 8 on the development of aluminized explosives.

1.12.1 Torpex-2[128,130]

This explosive, having the composition 42/40/18 RDX-TNT-Al, was developed by the British for use as a cast filling for underwater weapons. Torpex-2 is made by adding the appropriate amounts of TNT and aluminum to Composition B; accordingly, Torpex-2 made in this country contains about 0.6% of Bruceton Wax No. 10. Studies have been made of the flow properties of Torpex-2 and of the effects of wax, of aluminum grist and purity on the sensitivity of the explosive. It was not possible to detect any sensitizing effect of alloyed impurities in the aluminum. However, a close dependence of bullet sensitivity on aluminum grist was observed. The coarser the aluminimum the less sensitive the Torpex-2.

1.12.2 HBX

In England a mixture known as D-I or PNL was developed for the purpose of desensitizing Torpex-2 and certain other high explosives. The mixture has the composition 84/14/2 paraffin-nitrocellulose (12% nitrogen; ½ sec viscosity)-lecithin, the nitrocellulose and lecithin serving as emulsifying agents for the wax. Torpex-2, containing 5 parts of D-I, is known as Torpex D-I. In this country the effectiveness of D-I as a desensitizer was recognized, but there was reluctance to use it for two reasons: the danger of exudation of wax on hot storage, and the danger of decomposition of the nitrocellulose which, by contrast with the high-explosive ingredients present, is a relatively unstable material.

Extensive studies were made of higher melting petroleum-base waxes as substitutes for the low-melting paraffin used in D-I. As a result of these studies several available waxes and blends of waxes have been recommended which give good desensitization with very little exudation. HBX, which differs from Torpex D-I only in the substitution of a higher melting petroleum-base wax for the 135 F paraffin, has been adopted by the U. S. Navy.[125,130,131]

Another investigation showed that Vinylseal MA-28-14 was an excellent substitute for nitrocellulose and lecithin for emulsifying the wax in HBX.[132] This development, together with that detailed in the preceding paragraph, makes possible the preparation of a desensitized Torpex that does not exude on hot storage and that does not contain such an unstable ingredient as nitrocellulose.

Finally, extensive studies were made of the sensitivity of HBX, both in comparison with other explosives and as a function of such variables as aluminum grist and agglomeration. As with Torpex-2 coarser aluminum gives a less sensitive product. Light agglomeration of the aluminum acts the same way.[130]

[x]This section is based on reports prepared by E. H. Eyster and Frank H. Westheimer.

1.12.3 Baronal

This explosive, which has the composition 50/35/15 $Ba(NO_3)_2$-TNT-Al, was developed as a castable filling for underwater munitions. The mixture has a cast density of 2.27 g per cc and is almost equal to Torpex-2 in underwater performance on a *volume* basis. It was hoped that the mixture would be much less sensitive than Torpex-2. Surprisingly enough, Baronal was found to be in the same general sensitivity class as Torpex-2, and Torpex-2 rather than Baronal was adopted as an underwater charge.[133]

1.12.4 Miscellaneous Aluminized Explosives

Aluminized Composition A's have been prepared and briefly studied. They are made by adding atomized aluminum to Composition A-3 just after the wax has been added to the RDX-water slurry. The composition 73/9/18 RDX-wax-Al was considered for press loading into shells; and the composition 70/5/25 RDX-wax-Al was pellet-loaded in a Tritonal matrix so that the overall charge had the same composition as Torpex-2.[124,134-136]

Some study has been made of the pouring properties of the Tritonals, particularly of the segregation of aluminum in 80/20 Tritonal castings. 40/60 Tritonal can be detonated. Both 80/20 and 40/60 Tritonal can be appreciably desensitized by the addition of 5 parts of desensitizer D-2. The use of coarse aluminum desensitizes 80/20 Tritonal.[137]

Dentex, 48/34/18 RDX-DNT-Al, was developed as a substitute for Torpex-2. Its underwater performance is somewhat inferior to that of Torpex-2, but its sensitivity is significantly lower. However, this advantage was offset by the development of Torpex D-I and HBX, which are more powerful and less sensitive than Dentex.

Pentonal, 47/33/20 PETN-TNT-Al, is very sensitive to bullets. Torpex-2 analogs in which the RDX was replaced by Haleite and by Fivonite showed good performance.

1.12.5 Gas Evolution from Aluminized Explosives

The extensive use of aluminized explosives has revealed two difficulties peculiar to this type of filling; both result from the evolution of gas from the explosive. The first is known as spewing. Gas liberated from the molten explosive causes the rapid ejection of some of the material from the container during filling operations. The second is known as gassing. It is the evolution of gas from the solid explosive in a filled munition. Gassing can result in deformation of the booster cavities and battery cases in mines, and, when the gas is inflammable, it creates a fire hazard. Spewing has been observed principally with Minol; gassing is more serious with Torpex. Since Minol is not loaded in this country, spewing is not a serious problem here. The gassing of Torpex-filled stores is serious, however, and the succeeding paragraphs describe the successful methods developed to prevent gassing of Torpex and, incidentally, DBX and Tritonal.

The gas evolution from Torpex results from the presence of water in the explosive. The water is introduced with the Composition B which is made from water-wet RDX. It has proved impractical to dry Composition B, or to coat the aluminum in Torpex so that it will not react with water. Consequently, it has been found necessary to dry the Torpex itself. Attempts to do this by increasing the time of batching the Torpex failed. However, the addition of 0.5% of anhydrous calcium chloride to Torpex was successful. Torpex containing 0.5% of anhydrous calcium chloride generates little gas at elevated temperatures and essentially no gas at room temperature. Addition of calcium chloride introduces no new problems. Torpex containing 0.5% calcium chloride is indistinguishable from ordinary Torpex in sensitivity and stability. The calcium chloride makes the mixture very slightly hygroscopic, but the effect is small and the mixture is less than one per cent as hygroscopic as Minol. Torpex to which 0.5% of calcium chloride has been added has been adopted by the U. S. Navy.[138]

Tritonal will evolve gas when the explosive is wet. However, the ingredients from which Tritonal is made, TNT and aluminum, can easily be obtained free from moisture, so it should be possible to prepare dry Tritonal which will not generate gas. However, 0.5% of anhydrous calcium chloride will effectively stop the gassing of moist Tritonal.[139]

The gas evolution from Minol and DBX, both of which contain ammonium nitrate, can also be prevented. At low temperatures Minol, even when it contains several tenths of a per cent of water, does not generate much gas. The addition of a few per cent of anhydrous magnesium nitrate and 0.1% of stearoxyacetic acid reduces considerably the gas evolution from solid and from molten Minol at elevated temperatures. Similarly, the addition of 0.5% of anhydrous magnesium nitrate and 0.1% of stearoxyacetic acid stops the gas evolution from DBX.[140,141]

Chapter 2

THE PROPERTIES OF HIGH EXPLOSIVES

The work on the preparation of high explosives described in the preceding chapter required as a parallel activity an evaluation of the various candidate explosives prepared. For the most part these candidate explosives could be screened on the basis of tests of a relatively small number of properties — stability, power, sensitiveness to impact — tests which can be made with relatively small amounts of material. For the explosives which met these screening tests satisfactorily, further and more extensive testing was necessary. With both the preliminary and the subsequent tests, considerable work was necessary on the development of the testing methods themselves. Consequently the work described in this chapter deals both with the study of testing methods and with the results of the tests.

In addition to the testing program mentioned in the preceding paragraph and described in Sections 2.1 through 2.5, various other activities dealing with the properties of explosives were undertaken. Thus, in order to make the information available to investigators working on the synthesis of organic explosives and on their applications, a compilation of data on the properties of organic explosives was prepared. The data include physical properties, methods of preparation, explosive properties, and stability. The emphasis in the compilation was on high explosives rather than primers or detonators, and on pure compounds rather than mixtures. The data were taken in part from the open literature beginning January 1, 1907, and in part from the following classified sources.

1. OSRD reports issued to January 1, 1944.[a]
2. British reports available in the NDRC files to January 1, 1944.
3. Canadian reports available in the NDRC files to January 1, 1944.
4. Records at the Picatinny Arsenal.
5. Records at the Naval Powder Factory, Indian Head, Maryland.
6. Information made available by E. I. du Pont de Nemours & Company.
7. Information made available by the Hercules Powder Company.

A number of reports on the properties of individual explosives or on a detailed comparison of two or three explosives were issued by Division 8. From the nature of the subject material it is not possible to give useful condensations of the content of these reports; we shall, therefore, simply name the subjects and refer to the reports: NENO and MNO;[1] Cyclotol, Ednatol, and Pentolite;[2] Fivonite and Fivonite Compositions;[3] and Minol and Torpex[4].

The effect of moderate heating on explosives is measured in a variety of tests designed to determine the stability of high explosives (see Section 2.1). A more immediately practical study was made of the "cooking-off" phenomenon, the explosion of shells which have been left in overheated guns. It was found that the explosions result from the detonation of mercuric fulminate which takes place when that material is heated to 135 C or higher. During the study the explosion temperatures of nearly twenty of the more commonly used high explosives and explosive compositions were determined.[5]

The effect of applying high pressures to explosives was examined,[6] and it was found that the common high explosives are not detonated by the isothermal application of hydrostatic pressures up to 50,000 kg per sq cm combined with shearing stresses up to the maximum which the explosives would support. Pressures up to 100,000 kg per sq cm could be applied slowly to TNT, ammonium picrate, and nitroguanidine without causing explosions.

An entirely different aspect of the study of the properties of high explosives was brought to light by the request for inert simulants of various explosives. The simulants, which must match the physical properties of a given explosive, are used as "stand-ins" for the explosive in making certain tests. Thus a simulant might be used as the filling for studying the effect of changes in design and material on the armor-piercing ability of an armor-piercing projectile. A mixture of 5% of Celite 535 (Johns-Manville Company) and 95% of Aroclor 2565 (Monsanto Chemical

[a] A. H. Blatt, OSRD-2014, February 1944. An earlier compilation by A. H. Blatt and Frank C. Whitmore, OSRD-1085, December 1942, was issued in order to make available as quickly as possible a part of the data. All the information in OSRD-1085 is given in the final report, OSRD-2014.

[redacted]

Company) proved to be a close simulant for HBX, as the data in Table 1 show.[7]

Table 1. Physical properties of HBX and HBX simulant.

Property	HBX	Simulant
Laboratory density g per cc	1.66	1.74
Compressive strength psi at density d	3,280 ±300/1.72	3,420 ± 200
Modulus of elasticity, dynes per sq cm at density d	$8.95 \times 10^{10}/1.69$	6.6×10^{10}
Specific heat cal per g per C	0.24 at 15 C	0.25 at 26 C
Impact strength (IZOD) ft-lb at density d	0.070	0.047/1.68

2.1 STABILITY[b]

All military high explosives possess at least reasonably good stability, otherwise they are not adopted for service use. In this respect the stability problem differs from the sensitivity problem to be discussed in the next section. There are service uses for sensitive explosives; there is no service use for an unstable explosive. Military high explosives must be and are stable to heat over a long period of time. It is desirable that they be stable to moisture as well, but this is by no means essential since the containers (shells, mines, rocket heads, etc.) for these explosives are tightly closed. The methods for testing the stability of high explosives which were used at the Explosives Research Laboratory are outlined below, together with data on the stability of some of the high explosives tested there. Only cursory testing was done on most of the standard explosives of recognized stability such as ammonium picrate, picric acid, amatol and the like.

2.1.1 Tests

Tests used at the Explosives Research Laboratory were in part well-known tests carried out as described in the open literature. In part, however, modified apparatus and modified procedures were used, and reference should be made to the original reports for details.[8,9]

Purity

Since all pure samples of a particular high explosive behave alike, once the general stability of an explosive has been established it is only necessary to determine that subsequent samples are pure. The customary criteria of purity are melting point, and either acidity or basicity or pH. Many explosives, for example tetryl, are unfavorably affected by small amounts of acids or bases as impurities, and service samples of these materials must be essentially neutral. Observations of the color and odor of samples of explosives will often give preliminary indications of purity or, rather, indications of gross impurity.

International Test

The sample is heated in an open vessel for forty-eight hours at 75 C. Changes in appearance or weight are noted. The test serves to eliminate excessively volatile explosives.

Thermal Stability

The sample is heated in a loosely stoppered glass tube with a piece of methyl violet paper above the surface of the explosive. The test is run at 100 C and at 135 C for five hours. The time required for the color of the methyl violet paper to change to a bright salmon pink, and the time required for the sample to explode are noted if either of these events occurs within the five-hour period. This test serves to eliminate explosives of very inferior stability.

Hygroscopicity

The sample is exposed to atmospheres of various high relative humidities in a vacuum desiccator at room temperature for five days, or until equilibrium is established if this requires more than five days. The gain or loss in weight of the sample is noted. Some military explosives (in particular those such as amatol or Minol which contain ammonium nitrate) are quite hygroscopic. This does not necessarily exclude them from service use. However, hygroscopicity is always a disadvantage and does eliminate an explosive for some uses. Other things being equal, a nonhygroscopic explosive is preferable to one which is hygroscopic.

Vacuum Stability

This test measures the amount of gas liberated from a sample of explosive of specified weight when it is heated in a vacuum at an elevated temperature for a limited time. The usual sample is five grams; the test is ordinarily run at 100, 120, or 150 C, and the duration of the test is usually from twenty-four to forty-eight hours. The apparatus used at the Explosives Research Laboratory differs from that described in

[b] This section is constructed from information supplied by Frank H. Westheimer.

the literature, and the original reports should be consulted for details of construction and operation.

It is customary to deduct the gas evolved during the first ninety minutes of the vacuum stability test on the ground that most of it is probably occluded gas, and not gas produced by decomposition of the explosive. In general, a normal value for the vacuum stability test can be established for each explosive; larger amounts of gas evolved from subsequent samples indicate that they are of inferior quality. Comparisons of one explosive with another on the basis of vacuum stability tests are misleading, and often there is no correlation between vacuum stability tests at 120 C and those at service temperatures (−40 to +60 C).

Explosion Temperature

There is no generally accepted method of determining the temperature at which a material explodes. Two methods have been used at the Explosives Research Laboratory. In the first, five- to ten-milligram samples of the explosive are dropped onto the surface of a Wood's metal bath. The initial temperature of the bath is 360 C. The bath is allowed to cool and tests are continued until the lowest temperature at which the sample will deflagrate or explode in five seconds is found. The second method was devised to eliminate several sources of error in the first procedure. In the second method, the sample is placed in a copper tube which dips into the Wood's metal bath. When the sample deflagrates or explodes, the cover is blown off the copper tube. This breaks an electric circuit leading to an impulse counter and interval timer, thus giving an accurate measurement of the time during which the explosive was heated. The use of the copper cup ensures that the sample is in contact with the interior of the bath.[10]

Surveillance

The best test for the stability of an explosive which has yet been devised, exclusive of actual service, is surveillance. A sample of the explosive is maintained for a considerable period of time at a temperature as high as or higher than it will ever be subjected to in service. Portions of the sample are withdrawn periodically and examined for melting point or vacuum stability. The usual surveillance temperature is 65.5 C (150 F), although surveillance is occasionally carried out at both higher and lower temperatures. Most military high explosives will survive surveillance at 65.5 C for many years, and it can, therefore, be anticipated that they will be satisfactory for an indefinite length of time at ordinary service temperatures. The most stable explosives tested at the Explosives Research Laboratory were TNT and RDX, both of which survived without apparent change for over three years at 85 C. TNT is molten at this temperature. By contrast, some samples of PETN have failed in surveillance at 65 C in less than a year and a half. Even this surveillance life at 65 C, however, is ample assurance of adequate service life.

Table 2 gives surveillance and vacuum stability data on a number of service fillings.

2.1.2 Special Stability Problems

There are many special stability problems presented by individual high explosives. These problems (for

Table 2. Surveillance and vacuum stability data on some service fillings.*

Explosive	Composition	Surveillance Temp (C)	Surveillance Time (months)	Normal vacuum stability at 120 C Gas evolved (cc/5 g/48 hr)
PETN		65	17 to 29†	1.0 to 5.0 cc/2.3 g/20 hr
Pentolite	PETN/TNT—50/50	65	29†	3.0 at 100 C
Haleite		65	33†	4.5
TNT		65	23†	0.2
		85	23†	
RDX		65	32†	0.5 cc/5 g/24 hr at 150 C (‡)
		85	32†	2.0 cc/5 g/24 hr at 150 C (§)
Composition A	RDX/Wax—91/9	65	10†	0.7
Composition B	RDX/TNT/Wax—59.5/39.5/1	65	39†	1.0
Tritonal	TNT/Al—80/20	65	25†	0.2
Torpex-2	Comp B/TNT/Al—70/12/18	65	30†	
Minol	TNT/NH_4NO_3/Al—40/40/20	65	17†	2.0

*The data in this table are a selection from the data accumulated at the Explosives Research Laboratory. Additional data will be found in references 17, 58–60.

†Samples still in surveillance.

‡RDX made by the direct nitrolysis of hexamine.

§RDX(B) made by the combination process.

example, the factors which affect the stability of a particular explosive, the mechanism of decomposition of a particular explosive, and the selection of tests which will best measure the stability of a particular explosive) must be studied individually and are not amenable to routine testing. Three such special problems are considered in the paragraphs which follow.

Certain samples of Pentolite show highly erratic behavior on surveillance. As the result of an extended study of the reasons for this behavior, it was found that the stability of Pentolite is impaired by the presence of acid and, to a greater extent, by the presence of alkali. Nitrated by-products from the pentaerythritol synthesis, e.g., DiPEHN, have no detectable effect on the stability of Pentolite.

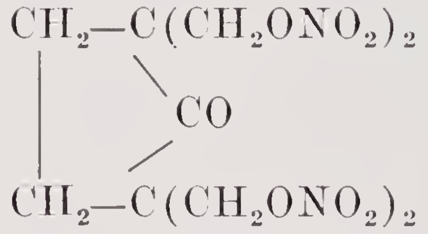
Contamination of Pentolite by acid is unlikely if the PETN from which it is made has been properly stabilized. Contamination of Pentolite by alkali is due to the alkali left in the PETN during ordinary procedure for the stabilization of the latter material. When PETN is stabilized by the addition of solid sodium carbonate to an acetone solution of the explosive, the PETN will contain about 0.03% of sodium carbonate. When sodium carbonate solution is added to an acetone solution of PETN, the precipitated material will contain about 0.008% of sodium carbonate. The addition of a 1% solution of ammonium carbonate to an acetone solution of PETN precipitates material which yields the highest quality Pentolite.

The 100 C vacuum stability test fails to reveal the presence of harmful amounts of alkali in Pentolite, since the temperature coefficient of the alkali-catalyzed decomposition is much smaller than that of the spontaneous decomposition. Nor does the 120 C vacuum stability test give useful information about the stability of the material; for the results of this test are largely determined by the amount and location of occlusions containing acetone, and these occlusions do not impair significantly the low-temperature stability of Pentolite.[11,12] The rate of gas evolution at 68 C is the best measure of the stability of Pentolite.[c]

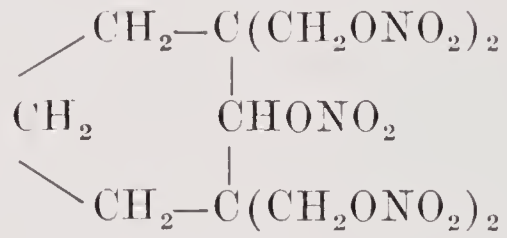
The stability of Haleite, ethylenedinitramine, has also been examined in considerable detail.[14] The decomposition of Haleite furnishes ethylene glycol, acetaldehyde, and nitrous oxide. When the solid explosive decomposes between 120 and 150 C, 90% of the decomposition products are volatile. The decomposition is not gas catalyzed; the temperature coefficient of the decomposition increases with increasing temperature in the range 100 to 145 C, and the rate of decomposition is increased by the presence of any one of a number of inert materials, for example, iron, iron oxide, barium sulfate, sand, or activated carbon. Large crystals of Haleite decompose more slowly than small crystals in the vacuum stability test, whereas large samples decompose more rapidly than small samples. When Haleite is crystallized, the more acidic the solvent the less stable is the product. The 135 C thermal stability test, useful with organic nitrates, is not useful with Haleite, for this material loses its nitrogen as nitrous oxide. The 120 C vacuum stability test does give useful results if appropriate precautions are taken.

The kinetics of decomposition of four organic high explosives have been studied.[15] The explosives were:

Fivonite



Sixolite



MNO

$CON(NO_2)CH_3$
|
$CON(NO_2)CH_3$

NENO

$CON(NO_2)CH_2CH_2ONO_2$
|
$CON(NO_2)CH_2CH_2ONO_2$

The investigation was carried out by measuring the gas evolved from the explosive. In some runs the decomposition was carried to completion, and the amount of gas produced per mole of the explosive determined. The rate of decomposition of Fivonite and Sixolite increases with time; the increase in rate with time is greater at moderate (85 to 120 C) than at elevated (135 to 150 C) temperatures. At the high temperatures the decompositions were followed to completion. The increase in rate with time for these nitric acid esters may well be due to autocatalysis. The possibility has, however, been suggested that some if not all of the effect is due to the fact that these are explosives with many reactive groups, and the appearance of autocatalysis can be produced by a multistep decomposition. By contrast, the decomposition of the nitramines in solution followed a simple first order law. The reactions take place at the same

[c] A related report[13] describes the preparation, optical crystallography, and fusion analyses of pure PETN and DiPEHN, together with a phase study of the system PETN-DiPEHN.

rate whether the explosives are molten or dissolved in TNT. The solid explosive decomposes much more slowly, however, and the acceleration in rate usually observed when an explosive is mixed with TNT has been correlated with the enhanced rate of decomposition in solution as compared with that in the solid state.

The activation energy for the initial decomposition of the nitric acid esters was about 50,000 cal per mole, whereas that for the nitramines was only about 35,000 cal per mole.

2.2 SENSITIVENESS[d]

New explosives and explosive mixtures are generally developed in the laboratory for specific field uses, and must accordingly meet certain requirements of sensitivity and performance. The ultimate tests of these properties are provided, of course, by actual trials in the munitions for which the explosives are intended, first on an experimental basis at a proving ground, and finally in combat. For these ultimate tests there is no substitute; but since they are time-consuming, expensive, and hazardous, all possible efforts are made to screen out, at the laboratory stage, materials which appear unlikely to pass service tests. Such laboratory screening tests may occasionally pass materials later rejected, or may occasionally hold back from final tests materials which might have been acceptable; nevertheless, their usefulness, within their proper domain, is great. The fact that most explosives under development are planned as substitutes for ones in use permits comparisons to be made between pairs of explosives in laboratory tests; from such laboratory comparisons the suitability of the substitute explosive must be inferred.

2.2.1 Sensitiveness Tests at the Explosives Research Laboratory[16-25]

In laboratory tests of sensitivity, pairs of explosives are compared by subjecting each explosive to stimuli (usually mechanical) of controlled violence, under controlled conditions, and comparing their responses. When these responses vary only in degree, the relative sensitivities may then be at once inferred, when account is taken of the statistical nature of these responses; but when the responses differ also in kind, then arbitrary decisions concerning the relative hazards of the various kinds of response must be made if a definite sensitivity comparison is demanded.

[d]This discussion is taken from a summary prepared by E. H. Eyster.

Drop-Weight Impact Tests

Drop-weight impact tests provide one of the easiest sensitivity comparisons which may be made. In such tests small samples of the explosives to be tested are loaded between a hardened steel anvil and plunger (the *tools*) and the plunger is then struck by a weight which is allowed to fall through a predetermined distance. By carrying out a series of trials at different drop heights, the probability of explosion as a function of drop height may be explored for the explosives to be compared. The 50% explosion height has been used at the Explosives Research Laboratory to characterize the results of such tests, and statistically efficient methods have been devised to determine this height and to estimate the random errors made in its determination. If, then, the 50% explosion height for one explosive is shown to be significantly higher than that of a second, the first explosive is shown by this test to be less sensitive than the second. In this manner many explosives may and have been ordered in *impact sensitivity*. It has been found, however, that *the ordering obtained depends upon the exact mechanical design of the tools used in the impact machine.* About a dozen different tool designs have been studied. Of these the following three have been particularly useful for testing solids, and have been extensively used at the Explosives Research Laboratory.

Type 3. In this design the explosive is loaded in a brass cup, 0.308 in. in inside diameter, 0.01 in. thick, and ⅞ in. high. The half-inch steel plunger tapers to a 0.306-in. diameter cylinder near the tip and fits inside the cup. The cup rests on a flat steel anvil. A 5-kg weight and a maximum drop of about 100 cm are used with these tools.

Type 5. In this design the explosive is loaded in a cylindrical cavity, $\frac{1}{16}$ in. deep and 0.376 in. in diameter, in the hardened steel anvil, and is covered by a sheet of thin tinfoil. The ½-in. plunger in this case tapers at the end to a 0.375-in. cylindrical section and is pressed down on the explosive in the cavity. A 5-kg weight and a maximum fall of about 100 cm have been used with this design.

Type 12. In this design the explosive is loaded on a square of 5/0 Flint paper, resting on a 1¼-in. hardened steel flat anvil. The plunger is a flat 1¼-in. cylinder. A 2½-kg weight and a maximum fall of about 330 cm have been used with this design.

The Type 3 design is suited particularly to the test-

ing of explosives of sensitivity equal to or greater than that of Tetryl. The other two designs will fire TNT, Composition A, and ammonium picrate. The sensitivity orderings produced by these three tool designs are not identical, though they do show a gross correlation. Apparently variations of the physical conditions (strength of confinement, effect of grit, etc.) during impact do not produce uniform changes in the apparent sensitivities of all explosives. At the Explosives Research Laboratory it is preferred, generally, to make important impact-test comparisons with several tool designs; when all agree in ordering, the results are satisfactory, otherwise different tests are appealed to.

Some typical results of impact tests with these three tool designs are given in Table 3.

TABLE 3. Sensitiveness of high explosives.*

1	2	3			4				5		6
	Dens.	Impact sens.			Bullet sens.				Shell imp. sens.		Booster
Explosive	(g/cc)	#3	#5	#12	I.I. (ord)	No.	I.I. (alz)	No.	V_{50}(fps)	σV_{50}	sens.
Aluminized Comp. A	1.71(p)	..	..	62	..	..					
Amatol 80/20	..	..	..	..	..						
Amatol 60/40	..	..	..	..	..						
Amatol 50/50	1.55(c)	..	..	101	>58	10					
Ammonium Picrate	1.55(p)	80	19	235	..						5‖20+2
Baronal	2.32(c)	84	..	..	..						10‖5
Borotorpex (46/44/10)	1.74(c)	..	..	..							
Comp. A-3	1.61(p)	>90	..	80	..						20 + 2‖15 + 2
Comp. A-12% Wax	1.58(p)	..	..	108	..						
Comp. A/KNO_3-50/50	1.76(p)	66	..	59	..						
Comp. B	1.69(c)	>90	26	82	50	579			209	8	
Comp. C-2	1.57(pl)	..	..	..	..						
Cyclotol-60/40	1.69(c)	..	..	78	38	225					5‖25 + 2
Cyclotol-70/30	1.72(c)	..	..	56	40	30					
DBX	1.76(c)	..	..	73	..		35	23			5‖25 + 2
Diethylene glycol dinitrate	Liquid	..	..	..	..						
DINA	1.58(c)	27	13	23	6	10					
Haleite	1.76(cr)	65	35	38	..						5 + 2‖20 + 3
Ednatol 50/50	1.62(c)	..	..	74(55/45)	69(55/45)	178					10‖5
Ednatol 60/40	1.62(c)										
Fivonite	1.59(c)	>90	38	69	42	58					5‖25 + 2
RDX/Fivonite 53/47	1.66(c)	..	..	29	27	40					
HBX	1.73(c)	..	..	130			70	570	411	Average of 4 tests	
Hexanitrodiphenylamine	..	..	..	..	..						
Minol-II	1.71(c)	..	..	76	..		35	44	828	28	15‖10
MNO		>90	39	103	..						
NENO		45	..	29	..						
Nitroguanidine	1.50(p)	..	..	>337	..						
Pentolite 50/50	1.65(c)	65	31	38	19	220			∽170		25 + 3‖20 + 3
PEP-2	1.42(pl)	..	..	..	..						
PETN	1.76(cr)	29	8	12	..						Fired by 5 + 3
Picratol 52/48	1.63(c)	..	..	210	95	20					
Picric Acid	1.60(c)	>90	22	54	27	11					5‖25 + 2
PTX-1	1.68(c)	..	..	46	..						
PTX-2	1.70(c)	..	..	38	8	14					
RDX	1.82(cr)	48	23	17	..						15 + 3‖10 + 3
RIPE	1.37(pl)	..	..	341	..						
Tetryl	1.56(p)	56	20	42	..						5 + 2‖20 + 3
Tetrytol 75/25	1.66(c)	..	..	70	43	40					25 + 2‖20 + 2(70/30)
TNT D-2	1.55(c)	..	..	311	>85	20					
Torpex-II	1.81(c)	>90	..	78			32	166	185	9	5‖25 + 2
Tritonal 80/20	1.75(c)	..	..	138			60	70	509	82	15‖10(85/15)
Tritonal 80/20,D-2	1.67(c)	..	..	271	..		..				
TNT	1.60(c)	>90	48	171	72	86			Over 1100		20‖15

*Data from the Explosives Research Laboratory.

BULLET-IMPACT TESTS

The bullet-impact test is performed by loading the explosives to be compared into suitable containers and firing at them with .30- or .50-caliber bullets (usually Ball, M2). When a suitable bullet-container combination has been found, the comparison is made with as many trials as seem warranted. From the results one may deduce whether the explosives display significantly different probabilities of explosion. This test is more difficult to carry out than is the impact test and requires much larger samples of explosive, but it is also more closely related to real hazards in combat. It has been found that the addition of aluminum powder to explosives changes the nature of their reaction to bullet impact, greatly increasing the chance of a mild partial explosion, but apparently decreasing the chance of high-order detonation. This makes it rather difficult to express sensitivity comparisons between aluminized explosives and nonaluminized ones. Within each class, however, comparison may readily be made, and these results may be expressed on a numerical scale as insensitivity indices. The indices for aluminized explosives should not be compared with those for ordinary explosives.

Typical sensitivity indices are given in Table 3.

THE SHELL-IMPACT TEST

There is great need for a test that will give information about the relative sensitivities of different explosives when they are loaded in bombs and the bombs are dropped from planes. The large-scale drop testing of bombs which should furnish this information is extremely expensive if enough tests are made to give statistically useful information; and, because of the many variables involved (terminal velocity, angle of incidence, nature of surface, etc.) the number of drops required in order to secure significant results is very large. The shell-impact test was developed to stimulate an a small scale conditions existing in the large-scale drop tests of bombs. Unfuzed 60-mm mortar shells, loaded with the explosives to be compared are fired at predetermined velocities (from 180 to 1,100 fps) against heavy armor plate. Testing is continued until the 50% explosion velocity has been determined with suitable precision. This test has not been developed so far as have the tests described earlier, but it is a test which shows sufficient promise to merit further development.

THE BOOSTER-SENSITIVITY TEST

This test was designed to measure the relative ease with which explosives could be brought to full detonation by boosters and involves testing 1-in. cylinders 1 in. high with a series of graded boosters. This booster series was prepared in the following way. The most powerful boosters are 1-in. diameter Tetryl pellets of 5, 10, 15, 20, and 25 g weight; the boosters of intermediate power are these same pellets separated from the charge by cylinders of Acrawax B 2 cm in height; the least powerful boosters are the same pellets separated from the charge by 3 cm of Acrawax B. Each booster may be identified by stating the weight of Tetryl and the thickness of wax: $5 + 3$ thus means a 5 g booster and 3 cm of wax. High-order detonation is detected by detonating the test cylinders on a ½-in. steel plate and inspecting the damage. Test results are expressed by naming the strongest booster that fails to detonate the test cylinder, and the weakest booster that does detonate it. The booster pair may be abbreviated thus: $15 + 3||10 + 3$. Naturally, the booster sensitivity depends upon the physical state of the sample. Cast cylinders are usually less sensitive than pressed ones. In a gross sense the results of this test also correlate with those of impact and bullet tests, but there are again exceptions, e.g., Minol-2 has very low booster sensitivity, although its bullet and impact sensitivity seem fairly high. All of these aspects of sensitivity must be considered in interpreting small-scale tests.

2.2.2 Sensitiveness Studies at the Hercules Experiment Station[26-32]

From July 1, 1942, until August 31, 1945, under Contract OEMsr-719 Division 8 supported an investigation of the sensitiveness of high explosives at the Hercules Powder Company. The Hercules group did not have to run routine sensitiveness tests and were able to devote their entire time to a study of sensitiveness. Their investigation was primarily an experimental study of the influence of a variety of factors on the sensitiveness of explosives to a number of different initiating influences.[e]

In the investigation a markedly improved friction pendulum and a considerably improved minimum-priming charge test were developed. Improvements were made in the rifle bullet test and modifications were made in the impact test equipment. It is recommended, as a result of the investigation, that new explosives be subjected to impact tests, to friction-pendulum tests, to minimum-priming charge tests, and to rifle bullet tests; and that the evaluation of

[e] This summary is based largely on OSRD-6629.

the sensitiveness of the explosive and the hazards involved in its use be made from the results of the four sets of tests rather than from any one test alone. Table 4 gives test data on a number of important explosives.

Sensitiveness to Impact

For most of the work a Bureau of Mines type impact machine was employed with a maximum height of fall of 100 cm and equipped with 1-, 2-, and 5-kg weights. This was later supplemented by a larger impact machine giving heights up to 200 cm. Impacts were usually run with one of the following hammer-and-anvil combinations:

- Design 1 — 1-in. diameter flat anvil, 0.5-in. diameter flat hammer.
- Design 1A — Same, but surfaces roughened by sand-blasting with No. 30 corundum.
- Design 2 — Anvil as in design 1. 0.306-in. diameter hammer, explosive placed in a 0.308-in. diameter copper cup which rested on anvil.
- Design 5 — Anvil as in design 1. Explosive placed in a 0.307- by $\frac{1}{16}$-in. cavity in a 0.5-in. diameter by 0.25-in. steel cylinder which rested on anvil. Hammer, 0.306-in. diameter.

The designs most adaptable to use for a wide variety of explosives are 1A and 5. However, all four were used rather extensively in addition to one or two others. Hammers and anvils were of tool steel hardened to Rockwell C 60.

One of the most important discoveries was the effect of thickness of explosive layer on the sensitiveness results. Actually, the mass of the explosive sample is the important variable rather than the thickness. Thus, the height of fall is very little affected when PETN or nitromannite is precompressed up to 24,000 psi. Other evidence shows that the mass of the sample taken, rather than its volume, is decisive: heavier impacts are required for larger samples. Hence sample weights should always be specified. Two samples of the same explosive of differing bulk density will give the same results if their weights are the same but not their volumes. For explosives of low melting point the effect of quantity of explosive on height of fall is small. Apparently the sample melts and enough is expelled to give a constant thickness.

Regardless of the design used (except for very rough sand-blasted surfaces) the graph of height of fall versus weight of explosive sample was always linear. A curious fact is the observation that for explosives such as PETN and nitromannite the height of fall apparently becomes independent of the weight as the thickness of the explosive layer on the anvil approaches zero. That is, the graphs of height versus quantity of explosive for 1-, 2-, and 5-kg weights come to a common intercept on the height axis. Thus for very thin layers the velocity of the falling weight, given by $\sqrt{2gh}$, rather than the energy, becomes the controlling factor. Originally Cyclonite did not appear to behave like PETN, as the intercepts for the different weights did not come at the same point; however, more recent samples of Cyclonite have been found to behave in the same way as PETN. Generally the results obeyed the law,

$$M(h - h_0) = \text{constant},$$

(M = mass of falling weight, h = height of fall for 50% shots, and h_0 = the intercept on the height axis for zero quantity of explosive.)

The addition of 5% of grit (Silex— 200-mesh silica) increased the sensitiveness of most high explosives by a factor of 6 to 10. Increased particle size of the explosive decreased its sensitiveness. Adiabatic compression of the air adjacent to the sample was without effect. Hardness of the impacting metals and rigidity of the anvil are of great importance as sensitiveness decreases markedly for softer metals or for even slight cushioning of the anvil. Initiation of the explosive apparently results from the compression of the explosive, from frictional effects between individual particles, and from flow across the metal surfaces. The most satisfactory hammer-and-anvil combination appears to be Design 5 in which even TNT can be brought within the range of a 2-kg weight on a 100-cm machine.

From a practical viewpoint it appears that impacts and frictional impacts even between relatively soft metals should be avoided, as should impacts under confinement. The presence of finely divided explosives, thin layers, etc., should be avoided as far as possible. Considerable hazards exist in the use of metals until their hardness becomes less than that of annealed copper; the hazards are markedly reduced for lead.

Sensitiveness to Friction

In investigating friction sensitiveness most of the work was carried out with a modification of the Bureau of Mines small friction pendulum, but two rotating pin arrangements were also investigated. In

the first, a small amount of explosive was mixed with Silex (a powdered silica) and ground under a rotating pin in a small copper cup. The second rotating-pin method involved grinding the explosive between a fixed anvil and a rotating pin to which pressure was applied with a hydraulic press. It was found that even with PETN, it was extremely difficult to cause shots with this apparatus, so its use was not further examined.

Because of the difficulties encountered with the rotating-pin method, all the rest of the friction work was carried out with a modified friction pendulum in which a narrow shoe or a ball bearing was used for the pendulum bob and fresh metal surfaces were used for each trial. By using sand-blasted surfaces it has been possible to extend the range of the machine to include not only initiating explosives but also explosives as insensitive as Tetryl and Composition B. Fresh surfaces are used for each trial.

In carrying out the friction tests one can use either sand-blasted surfaces for the anvil and the pendulum shoe, or use smooth surfaces and mix grit with the explosive. The pressure exerted on the anvil depends on the angle of incidence of the pendulum. It was found, however, that the height of fall generally decreased to a constant value when the angle of incidence exceeded a certain minimum, generally 2 to 4°, and then remained constant over the range tested, usually up to 10 to 12°. Loudness of shots is increased as the angle of incidence increases and as the area between contacting surfaces increases. The effect of increasing the pendulum weight is to decrease the height of fall continuously as the weight added to the pendulum is changed from 1 to 10 kg.

Rigidity of the anvil backing has little influence on sensitiveness. This is in contrast to the results obtained on an impact machine. Sensitization by grit is marked.

Increasing roughness of the pendulum and anvil results in a decreasing height of fall. The sensitiveness is independent of the thickness of the explosive layer until it becomes less than about 8 mg per square centimeter, apparently because the excess explosive is pushed out of the way by the pendulum so that, in effect, thickness is independent of the quantity of explosive used in a trial. Sensitiveness is not decreased for impacts between hardened steel and soft metals until one of the metals becomes softer than annealed copper. When both metals are the same there is a steady decrease in the hazard as the metals become softer.

Sensitiveness to Glancing Impact

A sliding rod machine in which a rod with a hemispherical nose slides down a trough and strikes the sample of explosive on an anvil was investigated in order to determine its usefulness. In this machine the height of fall for hardened steel nosepiece and anvil increases as the angle of impact comes closer to the vertical. For softer anvils, however, maximum hazard seems to occur at an angle of about 65 to 70°. The machine does not appear of much utility for military explosives less sensitive than Cyclonite, since it was not possible to secure audible shots or reproducible results with most such explosives. It does offer considerable utility in assessing the hazards of metals and other materials of construction.

Sensitiveness to Detonation by Initiating Explosives

An improved minimum priming charge test was developed. This test is a measure of the minimum weight of initiator required to detonate a charge of the explosive under study. Previously a primer had been used together with an intermediate wafer charge when necessary for insensitive explosives; the use of the wafer charge made comparisons between sensitive and insensitive explosives difficult. By employing as the primer a 40/60 mixture of lead azide and PETN it was possible to do away with the intermediate wafer charge; the lead azide-PETN primer will detonate insensitive as well as sensitive explosives.

Prior to the development of the azide-PETN primer, the minimum-priming charges of a large number of explosives, both pressed and cast, were determined by using a diazodinitrophenol primer with a PETN wafer charge when necessary. A very satisfactory correlation was observed between the impact sensitiveness as determined in the design 5 machine and the minimum priming charge for either the azide-PETN primer or the diazodinitrophenol primer with PETN wafer. The correlation was better with the azide-PETN primer. Since cast explosives are so much less sensitive than pressed, it is necessary to compare the two types separately.

Sensitiveness to Rifle Bullets

Extensive studies were made on various aspects of sensitiveness to rifle bullet impact. In these tests the container for the explosive was a short piece of pipe with a metal plate welded to one end. The explosive was then either cast or pressed into this container and a disk of steel or other material pressed firmly against

the surface of the explosive. This container was laid on its side with its base against a steel block and bullets were fired into the explosive through the disk along the axis of the container. This arrangement made it possible to study a number of factors influencing the production of detonations. The length of the explosive column did not greatly affect the sensitiveness to bullet impact. Increasing the diameter of the explosive column from one inch to two inches appeared to increase the proportion of partial detonations to complete detonations.

The influence of container material was extensively investigated. When only the disk through which the bullet penetrated was changed, detonations of 50/50 Pentolite were produced about as readily with copper as with mild steel, but somewhat less so with hard lead or Duralumin, and least readily with maple. In fact, maple gave about the same results as if there were no disk at all on top of the explosive. When, however, the base of the bomb was changed and bullets fired at the explosive with no disk on top of it, rather surprising results were obtained. Here the largest proportion of detonations occurred with maple and transite bases, and relatively few detonations resulted in the bombs with metal bases. It is thought this may be because the base of maple or transite was easily shattered by the bullet and the explosive forced against the steel backing block. When, however, the cylindrical casing wall was made of different materials with steel base and frontal disk, detonations were produced regularly with mild steel, monel metal, or Duralumin casings. Detonations occurred less frequently with yellow brass and copper, not at all with maple, and only occasionally with Phenolite or hard lead. This indicates that the side wall confinement of the charge is an important factor in the production of detonations. When the bomb was made entirely of a single material, all detonations were produced when made of steel and 50% with monel metal, very few detonations with Duralumin, yellow brass, or copper, and none at all with hard lead or Phenolite. When the whole bomb was made of maple there were, surprisingly enough, 30% detonations which possibly may be explained from the shattering action of the bullet on the maple base and the consequent impact on the steel backing block.

Maximum sensitiveness in the rifle bullet test occurs when the thickness of the metal pierced by the bullet before it hits the explosive is about $\frac{3}{16}$-inch. Soft-nosed bullets are more effective than armor-piercing and the latter are more likely to cause detonations if made with flattened noses. In small scale tests, liners of asphalt or other soft material appeared to decrease sensitiveness, although subsequent larger-scale tests on full-sized bombs showed little value for asphalt liners. There was not much difference in rifle bullet sensitiveness of cast explosives and pressed explosives at the same density.

TABLE 4. Sensitiveness of military explosives.

Height of fall (cm) necessary for 50% shots

			Friction pendulum: 30 mg sample, Sandblasted surfaces		Hercules sliding rod	Minimum priming charge (g)				Rifle-bullet test: Reg disk bomb, $\frac{3}{16}$-in. steel disk per cent detonations	
						Diazo initiator		PETN-lead azide initiator			
	Design 5 4 kg weight	Plane sandblasted surfaces 5 kg weight	2-in. ball 5 kg weight, 8° angle of incidence	2 in. x ⅛ in. ball, 4 kg weight, 4° angle of incidence	Sandblasted surfaces, 45° slide angle 10 lb rod 30 mg sample	Pressed (d = 1.4 g/cc)	Cast	Pressed (d= 1.4 g/cc)	Cast	Pressed	Cast
Ammonium Picrate	59	75	..	..	100	0.27	..	..	..	10	..
Amatol 50/50	..	..	..	..	22.5	0.25	0.57	..	..	0	0
Composition A3	46	29	..	..	..	0.21	..	..	..	..	..
Composition B2	38	61	16	31	9.5	.17	.27	..	.26	..	50
Composition B	38	54	16	38	100	.21	.33	..	.28	..	10
Cyclonite	23	25	18	25	10	.13	..	..	..	100	..
DBX	50	25	18	..	42	.19	.43	..	..	40	90
DINA	8	71	11	..	90	.15	.29	..	.20	..	..
EDNA	32	..	22	27	30	.19	..	..	..	90	100
Minol II	80	..	26	..	31	.27	.85	..	.42	..	80
Nitromannite	15	12	1.1	3	5.5	..	..	..	..	..	..
Pentolite 50/50	28	..	12	..	9	.13	.21	..	.16	20	100
PETN	16	19	7.5	11	9	.09	..	.04	..	100	..

2.3 PERFORMANCE[f]

At the Explosives Research Laboratory,[16,17,23] where essentially all of the work of Division 8[g] on the performance of high explosives was done, two tests were used for the laboratory-scale assessment of the *performance* or effectiveness of explosives. They are the ballistic mortar and plate-denting tests. The quantities measured by these two tests are called the power and the brisance, respectively. Other measurements, such as the determination of the velocity of detonation, the cavity-charge performance, and the fragment velocity, are in general related to performance, but only the first has been systematically measured for many explosives. It is discussed in Section 2.4.

Ballistic Mortar

The ballistic mortar has been systematically used in the Explosives Research Laboratory to determine the power of explosives and explosive mixtures. This is a standard instrument and has been described in the open literature. With the ballistic mortar one determines essentially the number of grams of TNT required to give the same deflection as 100 grams of the explosive under test; this value, called the power or TV (TNT value), is the expression of the test results. These values are generally somewhat different from those obtained in the Trauzl Lead Block Test, but the method is very convenient, and the results seem to be equally valid. Ballistic mortar values are particularly useful for new explosive substances. The mortar tends to exaggerate the effectiveness of materials containing large amounts of ammonium nitrate and perhaps does not fairly recognize the improvement in performance effected by aluminum powder. Some typical ballistic mortar values are given in Table 5.

The Plate-Denting Test

For certain materials, particularly plastic explosives, the conditions in the ballistic mortar seem to be rather remote from the conditions which will be encountered in use. For such explosives the contact effectiveness, or brisance, seems more important than the power. To measure this property we have used plate-denting tests, in which an essentially unconfined stick of explosive is detonated with its flat end in contact with a heavy steel plate. The depth of the dent made in the steel can usually be measured accurately and has been taken as a measure of the performance under these conditions. The density of the test cylinder is of great importance. For cast or plastic explosives this density is usually fixed and characteristic of the explosive, but for pressed materials it is not determined. Just how to treat such materials has not been settled. The practice at the Explosives Research Laboratory has been to prepare a cylinder of as high density as possible and to test it. The results are generally expressed as 100 times the ratio of the depth of dent produced by the test sample to that produced by a good TNT casting.

Typical plate-denting values are given in Table 5.

2.4 VELOCITY OF DETONATION[h]

The velocity of detonation is one of the few properties of high explosives capable of precise definition and measurement. The velocity of detonation can be calculated according to the hydrodynamic theory of detonation from the loading density, the equation of state of the product gases, and other purely thermal data.[33] If agreement between the observed and the calculated velocities is obtained over a range of loading densities, the equation of state assumed to apply to the product gases can be used with some confidence to estimate quantities such as the detonation pressure and the detonation temperature; quantities which are of more practical interest than the detonation velocity, but which are not at present capable of direct measurement.

In order to make the comparison between observed and calculated velocities, it is necessary to have detonation velocity data which are truly characteristic of the explosive. The hydrodynamic theory takes no account of the rate of chemical reaction in the detonation wave. Experimentally this finite rate of reaction exerts a marked effect on the measured detonation velocity unless care is taken to eliminate it. For an infinitely fast chemical reaction, the full thermodynamic detonation velocity is developed in a charge of any size; for a finite reaction rate, however, the full velocity is developed only if the charge diameter is sufficiently large so that the chemical decomposition in the center of the charge is completed before the pressure at that point is appreciably reduced by

[f] This section is taken from a summary prepared by E. H. Eyster.

[g] Division 8 considered only certain aspects of the performance of high explosives. The work of Division 8 should be supplemented by an examination of the work of Division 2, which was directly concerned with damage from high explosives.

[h] This section is based on a summary prepared by G. H. Messerly.

rarefaction waves originating at the surface of the charge.

It is fairly well established that the detonative decomposition of solid explosives takes place through the progressive destruction of surface layers of the component particles.[34] If the primary surface reaction is the rate-controlling step in this decomposition, the detonation velocity will, for charges smaller than the critical size, depend on the particle size of the charge material as well as the diameter of the charge.

Since the reaction rate depends on the detonation pressure, and this in turn on the density of the charge, the magnitude of the diameter and particle size effects are also functions of the charge density, being in general more pronounced in the lower density region.

In order to obtain data which are theoretically significant, effects of both charge diameter and particle size must be eliminated. A great deal of the experimental work on detonation velocities was directed toward this end. Charges of increasingly large diameter and decreasing grist size were fired in an

Table 5. Performance of high explosives.*

7		8		9		10		11		
Mortar (TNT = 100)		Brisance		Det. Vel.		Frag. Vel.		Stability		
		Dens.	Re. Br.	Dens.	Rate	Dens.	Vel. (rel) TNT = 100	Vac.	Therm.	Explosive
5	142	1.719	110	1.70	7800	1.696	113			Aluminized Comp. A
9	130			1.60	5200	1.655	73			Amatol—80/20
6	128			1.60	5900					Amatol—60/40
	123	1.552	52	1.60	6400			0.87(120)	N.A.	Amatol—50/50
5	99			1.55	7050					Ammonium Picrate
8	96			2.32	5450			0.00(120)	N.A.	Baronal
3	129	1.742	127	1.74	7600			5.47(120)	N.A.	Borotorpex (46/44/10)
11	135	1.611	126	1.60	8200	1.608	108			Comp. A-3
3	132			1.585	8240	1.566	109			Comp. A—12% Wax
2	98					1.757	92	0.08(120)	N.A.	Comp. A/KNO_3—50/30
29	133			1.68	7790			0.50(120)	N.A.	Comp. B
3	143	1.52	111	1.58	7800					Comp. C-2
14	133	1.716	132	1.68	7790	1.672	114	1.48(120)	N.A.	Cyclotol—60/40
3	135	1.725	136							Cyclotol—70/30
3	146	1.762	102	1.66	6700			0.60(100)	N.A.	DBX
7	127			1.375	6800					Diethylene glycol dinitrate
7	143			1.58	7650			5.01(100)		DINA
34	139			1.50	7550			3.21(120)	N.A.	Haleite
3	117	1.623	112(52/48)			1.600	104(55/45)	0.38(100)	N.A.	Ednatol—50/50
2	121			1.58	7330					Ednatol—60/40
16	121			1.57	7160			4.87(100)	55	Fivonite
	134							3.72(100)	60′	RDX/Fivonite—53/47
	133	1.730	106	1.735	7400	1.687	113	5.02(120)		HBX
6	115									Hexanitrodiphenylamine
3	143	1.719	NE(c)	1.70	6000			1.48(120)	N.A.	Minol—II
15	117			1.45	6850			0.84(100)	N.A.	MNO
14	135			1.63	7800			EC-5hr(100)	50′	NENO
3	104			1.50	7060					Nitroguanidine
31	126	1.662	121	1.63	7450	1.632	108	2.10(100)	45′	Pentolite—50/50
2	115			1.42	7540			0.0(100)	100′	PEP-2
34	145			1.60	7920			2.79(120)	135′	PETN
3	100	1.630	100	1.625	6915	1.618	99			Picratol—52/48
13	112			1.60	7080					Picric Acid
3	132	1.684	127			1.644	111			PTX-1
	138	1.712	141	1.685	7900	1.676	118			PTX-2
ca.100	150			1.60	8235			0.38-24(150)	N.A.	RDX
3	118	1.37	85	1.35	7320	1.395	102	0.14(120)		RIPE
51	130	1.592	115	1.55	7375					Tetryl
3	122	1.660	118							Tetrytol—75/25
3	100	1.550	96	1.57	6800	1.544	94			TNT D-2
11	134	1.829	120	1.80	7530	1.768(41/41/18)	116	0.64(120)	N.A.	Torpex—II
3	124	1.753	93	1.76	6770	1.82(70/30)	97	0.10(120)		Tritonal—80/20
3	123	1.667	85	1.68	6560	1.642	98			Tritonal—80/20,D-2
	(100)	1.602	(100)	1.60	6850					TNT

*Data from the Explosives Research Laboratory.

effort to demonstrate that the detonation velocities finally obtained were truly invariant to these specific influences.

The velocity work was performed with a rotating drum camera with a speed of 240 meters per second.[35,36] The camera consists of an aluminum alloy drum (in the shape of a shallow angel food cake pan) which carries on its inner circumference a meter length of 35-mm film. The drum is driven by a 30-rpm, 2-hp synchronous motor through an 8/1 speed increaser. Motor, speed increaser, and drum are inclosed in a 24-in. diameter pipe which is evacuated to 10-cm mercury to decrease the windage on the drum. The drum rotates in a vertical plane, and the image of a vertical cylindrical column of explosive is formed on the film on the inner circumference of the drum by means of an *f*2.0, 5-in. lens and a right angle prism. A 0.002-in. slit at 0.025 in. above the moving film cuts off all the image of the explosive charge except a narrow central portion, and thereby greatly increases the time resolution of the camera.

The explosive charge is fired in a light-tight, bombproof chamber, and viewed by the camera thru 3¼ inches of bullet-resisting glass. The detonation wave initiated at one end of the explosive charge is self-luminous, and the combined motion of the image of the detonation wave across the film and the longitudinal motion of the film produce a slanting line whose slope is simply related to the detonation wave velocity.

The first work done with this equipment furnished a variety of information on the nature of the detonation process. It was found that the luminosity of a detonating charge originates mainly in the intense shock wave produced by the detonation in the surrounding atmosphere.[37]

Various atmospheres differ markedly in their light-emitting character, an observation which led to the development of the explosive flash photography technique.[38] The duration and intensity of the luminous radiation emitted by detonating explosives is altered markedly by the presence or absence of a transparent covering on the charge, and by the spacing between such a covering and the surface of the charge. These results showed that the width of the luminous zone in detonating explosives is not a measure of the width of the reaction zone as had been sometimes assumed. As a matter of fact, later studies have shown that this statement is still true when the shock light is eliminated, and the radiation originating only within the detonating explosive is examined.[39]

The first detonation velocity results obtained with this equipment appear in reference 40. Most of the compounds reported were subsequently reinvestigated and their detonation velocity curves revised upward when it was found that maximum rates had not been attained.[41-43] The general conclusions arrived at in reference 40 have not been invalidated, however. The detonation velocities of most explosives are linear functions of the charge density in the density range 0.8 to 1.6, with a slope which averages 3,500 meters per second per density unit. The charge diameter and particle size effects are most serious in the lower density range, below 1.2, where larger diameter charges, and finer grist charge material are necessary to obtain the thermodynamic maximum velocity than for the more densely packed charges. The belief that high brisance is necessarily an attribute of high detonation velocity was shown to be not generally true.

A summary of all the detonation velocity data obtained at the Explosives Research Laboratory to the time of its closing is given in reference 41. Detonation velocity data for most of the common explosives are reported in considerable detail. For most of the explosives studied, it is believed that the curves given in that report approach closely to the full thermodynamic rate. A selection of the data is given in Table 5.

Attempts have been made to obtain an equation of state which would satisfactorily represent the experimental detonation velocity data for different kinds of explosives over a range of charge densities.[44,45] The experimental data used both in determining the parameters of the equation of state, and in testing the resulting equation were subsequently found not to represent the maximum velocities of the explosives considered. These data were from reference 40, and previous interim reports; and the rather indifferent results of the theoretical treatment may be attributed mainly to inadequacy of experimental data on which it was based, although there is also some question as to whether the form assumed for the equation of state is entirely correct. This subject could profitably be reconsidered with the newer velocity data now available.

In addition to the explosive compounds and mixtures which show the usual linear density-velocity relation two reports have treated the abnormal behavior of explosives containing ammonium nitrate[46] and of mixtures of ammonium picrate of different grist sizes.[47] The nitrate explosives show a normal rate in the low-density range and an abnormally low rate at higher density, and thus constitute an exception to

the usual case of maximum deviation from thermodynamic rate at low-charge density. A mixture of ammonium picrate of fine and coarse grist size was found to detonate at a lower rate than either the fine or coarse grist material alone. No satisfactory explanation of either phenomenon has been advanced.

Most of the detonation velocity studies were, as mentioned above, directed toward obtaining the true thermodynamic velocity of the various explosives. However, some work was done on a systematic study of the rate-diameter relationship which would permit an estimation of the detonation reaction zone length according to the theoretical developments of Jones and Eyring. The first results of this study have been reported.[48] Further studies would be very helpful in elucidating the nature and mechanism of the detonation process. For this purpose, however, it would be well to review the experimental procedure used in both the preparation of the charge and in the measurement of the velocity; since for the velocity-diameter studies to be most useful, the maximum experimental precision is required. In this connection it should be noted that the velocity data reported by Cybulski from the Safety in Mines Research Station at Buxton in England show considerably greater reproducibility than do the Bruceton data. It would be useful to investigate the apparatus and methods of Cybulski before further extensive velocity work is undertaken.

In addition to the reaction zone length studies there are reported in reference 48 the results of measurements of the detonation velocity of insufficiently boostered cased charges, which were undertaken in an attempt to determine the effect of low-order detonation on the fragmentation of the shell case, and studies on the steady-state shape of the detonation wave in various cylindrical explosive charges.

The significance of a number of experiments on the detonation velocity close to the point of initiation has been considered.[48,49]

2.5 HEATS OF COMBUSTION

The heats of combustion of some fifty nitrated organic compounds have been determined by burning the compounds in oxygen in a constant-volume calorimetric bomb. The accuracy of the combustion technique is better than 0.1%; errors due to impurities in the samples may be considerably larger, however. From the heats of combustion, the heats of formation were calculated; and, for those compounds of particular interest, the velocities of detonation were calculated according to the procedure described in reference 33.

Some preliminary rules were developed for predicting the heat of formation of nitrated organic compounds. An example will illustrate the procedure. The heat of formation of nitroethane, $CH_3CH_2NO_2$, is —33 kcal per mole. The heat of formation of ethane, CH_3CH_3, is —22 kcal per mole. The difference, —10 kcal per mole, is the change in the heat of formation accompanying the replacement of an aliphatic hydrogen atom by a nitro group. Similarly, the changes in the heat of formation accompanying (1) the replacement of a hydroxyl hydrogen atom by NO_2 ($OH \longrightarrow ONO_2$) is +25 kcal per mole; (2) the replacement of an aliphatic amino hydrogen atom by NO_2 ($—NH \longrightarrow —NNO_2$) is —7 kcal per mole; (3) the replacement of an aliphatic amino hydrogen atom by NO_2 when the amino group is attached to a phenyl group ($C_6H_5NH \longrightarrow C_6H_5NNO_2$) is +17 kcal per mole; and (4) the replacement of an amido hydrogen atom by NO_2 ($CONH \rightarrow CONNO_2$) is + 18 kcal per mole. Replacement of an aromatic hydrogen atom by a nitro group is not amenable to such simple treatment.[50,51]

In a later investigation[52] the heats of combustion of some twenty organic explosives were determined. The accuracy of the determinations was at least equal to that of the earlier work, and, since the purity of the samples was greater, the results are believed to be more reliable. Heats of combustion of eight extensively used explosives are given in Table 6. For experimental procedures and for results with the other sixty-odd explosives whose heats of combustion have been measured, reference should be made to the original reports.

TABLE 6. Heats of combustion.

Explosive	Molecular weight	Heat of combustion (kcal/mole at 1 atmosphere)
1. Ammonium picrate	246.14	674.76
2. Diethanolnitramine dinitrate DINA	240.14	573.69
3. Haleite (ethylenedinitramine)*	150.05	369.7
4. Hexanitrodiphenylamine hexanite*	439.04	1310.6
5. Nitroguanidine	104.07	207.15
6. Picric acid	229.12	611.93
7. Tetryl	287.15	836.78
8. TNT	227.13	814.30

*Data for compounds 3 and 4 are taken from OSRD 702.[51] Data for the other compounds are from OSRD 5306.[52]

2.6 IDENTIFICATION AND ANALYSIS

Four methods were applied to the analysis and identification of high explosives: color tests, polarography, microscopy, and chromatography. Chromatography was used particularly with RDX and related compounds; this application was discussed in Section 1.2. Microscopy as applied to individual high explosives has been mentioned in Sections 1.2, 1.3, and 1.4. The general applications of microscopy to high explosives and boosters are discussed below; applications to primer compositions are considered in Chapter 7.

The most widely applicable and simplest analytical procedure developed consists of eleven color tests which permit identification of sixteen well-known high explosives. The tests, which require only the simplest of apparatus, are applicable in the field as well as in the laboratory. The procedure is written in such a way as to enable the tests to be used by nontechnical personnel. The tests are also useful for the identification of eight widely used binary explosive mixtures; this, however, requires judgment and ingenuity on the part of the operator in selecting the proper order of application of the tests and in interpreting the results of the tests.[53]

An attempt was begun in the spring of 1943 to evaluate the usefulness of the polarograph as an analytical tool by a study of the polarographic behavior of some simple aromatic nitro compounds and of TNT, Tetryl, and picric acid. It was concluded that it would be possible to determine small amounts of the highly nitrated compounds when they were mixed with large amounts of less highly nitrated materials, but the reverse is generally not possible. Further, and more discouraging, it was not possible to distinguish with sufficient accuracy between two compounds of the same degree of nitration, for example, TNT and picric acid. Consequently the work was discontinued.[54] Much more success attended the investigation of primer mixtures which is described in Chapter 7. In the application of microscopy to the identification and analysis of explosives, thirty-two high explosives and boosters, selected after consultation with the Services, were examined as pure individuals and mixtures. Two methods were developed for the analysis of these compounds.[55]

The first procedure is based upon the classical methods of optical crystallography. It requires that the analyst have available complete data on the crystallographic properties of the compounds which are likely to be encountered in an unknown sample. Comparison of the crystallographic properties of the constituents of the unknown sample with those of known compounds is sufficient to establish the composition of the sample. All the crystallographic data on military explosives necessary for analysis by the optical crystallographic method are presented in reference 55.

The utility of the optical crystallographic method for analyzing simple or mixed explosives suffers from the fact that it is slow. Determination of the complete optical crystallographic properties of an organic compound may require anywhere from a few hours to a few days. Further, it requires that the analyst have expert training in optical crystallography.

The second procedure for the microscopical analysis of high explosives is the method of fusion analysis, which is not subject to the limitations noted for the optical crystallographic method. The fusion method also makes use of microscopical techniques but it can be employed by the average analyst, after a brief period of instruction, and permits a very rapid analysis with a few milligrams of the sample. The basis for the method was established by Lehmann in 1891 when he showed that an organic compound crystallizes from its own melt in a very characteristic fashion.[56] Further work in this field by McCrone had shown that the technique of fusion analysis is a most useful analytical method for certain types of organic compounds, particularly for some high explosives.[57]

The method of fusion analysis is the observation, usually with the microscope, of the behavior of an organic compound when heated slowly on a microscope slide under a cover glass up to its melting point, followed by slow cooling to room temperature. During this process it is usually possible to observe so many characteristic properties of the compound that identification may be established within a few minutes.

Observation of the properties of the crystal-front may often be facilitated by carrying out a mixed fusion of the sample with thymol. By this procedure rapid crystallization is retarded and the crystal-front is stabilized for a more leisurely examination. Other visible phenomena which may occur in the course of the fusion analysis are frequently useful in identifying the material. These include volume changes in cooling with the formation of characteristic shrinkage cracks, color and pleochroism, twinning, polymorphic transformations, and anomalous variation in polarization colors.

With the addition of a few modifications, the technique of fusion analysis has been successfully applied to the examination of more than forty high-explosive compositions which include the following: Alumatol, Amatex, Amatol, Baronal, Compositions A, B, and C, Ednatol, Ednatal, Minol, Minex, Pentolite, Pentonal, Schneiderite, Tetratol, Torpex, Trimonite.

In addition to obtaining information regarding the qualitative composition of the mixture it is frequently possible by microscopical methods to establish whether the sample is uniform in composition; whether it has a surface coating of wax, graphite, or the like; and whether the sample is cast or pressed. In addition the purity of the individual components may be assayed and the approximate percentage composition of the mixture may be determined.

Chapter 3

APPLICATIONS OF HIGH EXPLOSIVES

In this chapter are considered a variety of specific applications of high explosives. Most of these applications (Sections 3.1 to 3.6) utilize the shaped-charge effect, and an understanding of them will be helped by a careful study of Chapter 4, in which fundamental work on shaped charges is described. In addition there will be found in Sections 3.7 to 3.10 descriptions of such diverse topics as an improved hand grenade, explosive streamers, liquid explosives, and a procedure for increasing the brightness of shell bursts.

3.1 SHAPED-CHARGE BOMBS[a]

Since early in World War II there has been interest in the possibility of using the cavity effect in a large bomb for attack on massive targets. The targets most often considered were the heavy concrete submarine pens installed by the Germans at several places along the French coast, for these structures had proved to be invulnerable to attack by conventional and available bombs. However, two factors tended to make the use of cavity-charge bombs unattractive. One was the fact that, while the jet from such a bomb would have great penetrating power, it was problematical how much damage the jet would do to installations beyond the heavy concrete protection; the other was the necessity for scoring a direct hit if the jet was to have any chance of accomplishing its mission. Since the installation of a cavity in the nose of a bomb reduces its explosive capacity by 20 to 30 per cent, it was argued that all bombs so modified would suffer a loss of this amount in general blast effectiveness, while only a very small percentage would actually utilize the penetrating power of the jet. As a result of these considerations, development of shaped-charge bombs proceeded very slowly, although a few were constructed and tested.

In the fall of 1944, the Navy became interested in using shaped-charge bombs against warships. While the force of the arguments just mentioned was recognized, there were two reasons why the point of view had changed somewhat. As a result of experience with the bazooka and other shaped-charge devices, it was realized that most tanks put out of action by such weapons were damaged by the burning of the fuel supply or by an explosion of the ammunition caused by the jet rather than by direct mechanical action of the jet. It seemed reasonable to consider a warship as similar to a tank but on a larger scale. Although it is undoubtedly true that putting a hole through the decks of the ship would not put it out of action, an accompanying ignition of the fuel supply or explosion of the magazine might well do so. Furthermore the development of guided missiles had been proceeding successfully, and, by the use of a guiding device such as Razon, a high percentage of hits could be anticipated even against such a small target as a ship. As a result of considerations such as these the Navy requested that shaped-charge bombs in a variety of sizes be developed and procured on high priority. The highest priority was given to the 1,000-lb size since, by making it ballistically equivalent to the 1,000-lb GP bomb, it would be possible to equip it with guiding attachments which were already developed.

By agreement among representatives of the Navy Bureau of Ordnance, the Army Ordnance Department, and NDRC Division 8, the Ordnance Department undertook the procurement of a number of shaped-charge bombs in all sizes from 100 to 2,000 lb, using 60-degree drawn steel cones for the cavity liners. The Explosives Research Laboratory [ERL] of Division 8 undertook to carry out small-scale tests of various designs of bombs against various model ship targets and to design and procure bombs in the 1,000-lb size, using formed and welded 45-degree steel cones as the cavity liners. It was felt that 45-degree cones might have advantages, but that they could not be drawn easily. The Naval Proving Ground at Dahlgren agreed to test the full-scale bombs by firing them statically against spaced armor plate targets representing ship decks.

It had been hoped and expected when the program was started that the jet from the 1,000-lb bomb would perforate all the decks of a Japanese battleship and still have sufficient residual force to ignite fuel oil or explode ammunition. It was realized, however, that it is difficult to predict with any kind of precision the performance of a shaped-charge munition

[a]This section is taken from a report prepared by D. P. MacDougall.[1,2]

against such a complicated spaced plate target as a warship, although its performance against a single massive plate could be estimated very well. Small-scale ($\frac{1}{10}$ and $\frac{1}{5}$) tests carried out at ERL showed that the 1,000-lb shaped-charge bomb could be expected to defeat the deck system of a battleship if the bomb missed the superstructure and the jet had to penetrate only through the main decks. There was not much margin, however, and if the tests were carried out with the bomb separated from the main deck system by the three light decks of the superstructure, success could not be achieved. The amount of steel in the superstructure is quite small (three decks, each of $\frac{1}{2}$-in. mild steel), but if the bomb detonates on top of the superstructure the jet must travel 24 ft through air before it has a chance to work on the main part of the target. Although the performance of a cavity charge improves as the stand-off is increased from zero to two or three calibers, at greater stand-offs the performance decreases, presumably due to dispersion of the jet. Even the 2,000-lb size when tested on a model scale could not defeat the battleship target with superstructure.

The fuzing of a shaped-charge bomb presents a serious problem. In order to have any cavity action, detonation must be started at the rear of the charge. However, the standard tail fuzes are not fast enough to detonate the bomb with sufficient stand-off. In fact their use would result in detonating the bomb at zero stand-off or even with considerable distortion and crushing of the cavity liner. Two methods were considered for fuzing these bombs. One, adopted by the Army Ordnance Department, consisted of running Primacord from a nose fuze, set for superquick action, back through a central pipe to a booster at the rear of the charge. The other method, used in the bombs procured by the Explosives Research Laboratory, consisted of attaching a small (1-in. diameter by $2\frac{1}{2}$ in. long) shaped charge to a standard nose fuze (M103) and allowing the jet from this small shaped charge to shoot down a central pipe and strike a tetryl booster located near the rear of the bomb. The standard M103 fuze was used as the basis for this point-initiating, tail-detonating shaped-charge fuze not by choice, but because it was available. However, this fuze is very massive, and its use places several inches of metal in the path of the jet, the equivalent of adding several inches to the target. All ERL bombs tested were detonated by means of such a shaped-charge unit, which functioned properly every time. The Army bombs were detonated with the Primacord arrangement, which also functioned perfectly. The shaped-charge fuze makes loading and assembly somewhat easier than does the Primacord fuze, but care must be taken in cutting threads, etc., so that good alignment is obtained. Alignment is not so important with the Primacord fuze.

The ERL 1,000-lb bombs contained 45-degree steel cones having a wall thickness of $\frac{1}{2}$ in. These cones were made by forming in three longitudinal sections and then welding the sections together in a jig. The first cones made were annealed after welding but were not otherwise treated. Later bombs contained cones which had been formed from heavier plate, and which were then machined on a lathe to very close tolerances. The small number of tests conducted failed to reveal any significant difference in the performance of the two, but from other work we feel that it is worth while to machine the cones and obtain near geometrical perfection.

AN-M65 1,000-lb GP bomb cases were cut apart 10 in. back from the nose, and the cones were welded in place. The base of the cone was thus about 10 in. from the nose of the bomb. The bombs were loaded with about 430 lb of Composition B. This represents a 28% decrease in the load of 595 lb of Composition B contained in the standard AN-M65 1,000-lb bomb.

Full-scale 1,000-lb bombs procured both by the Explosives Research Laboratory and by Army Ordnance were tested statically at Dahlgren against target plate arrangements representing a battleship, both with and without superstructure. In some of the tests, the space representing the hold of the ship contained drums of diesel oil; in others this space contained bombs loaded with cast TNT. Against the target without superstructure, the results were generally successful; that is, the target was defeated and the oil set on fire or the bombs exploded. In agreement with the results of the model tests, the bombs could not defeat the target with superstructure. This is a very serious drawback to the effectiveness of these bombs, since over two-thirds of the deck area is covered by superstructure. In agreement also with the small-scale test results, the 2,000-lb shaped-charge bomb was ineffective against the target with superstructure.

By the time a limited number of bombs had been tested at Dahlgren, the Japanese Navy had just about run out of ships, and the ending of hostilities soon afterward made it unnecessary to decide upon the advisability of producing large numbers of shaped-charge bombs. Despite the fact that this type of bomb did not prove to be so effective as had been hoped in

terms of amount of penetration achieved, it was very successful in setting off explosives and in igniting fuel oil when the jet could get through the protecting plates. This weapon should receive further consideration before a final decision is made as to its usefulness.

A related development involves the addition of a shaped-charge head to a semi-armor-piercing bomb. In this weapon the shaped-charge is expected to do part of the job of penetrating the armored target. From the results of $\frac{1}{5}$ scale tests it was concluded that the addition of a shaped-charge head to the 500-lb SAP bomb would enable the weapon to penetrate 6 in. of homogeneous armor at a striking velocity of 750 fps as opposed to a penetration of 2.5 to 3 in. for the unassisted bomb. The chief weakness of the bomb would be its relative ineffectiveness against spaced armor, a weakness it shares with the bombs described earlier.[3]

3.2 ANTISUBMARINE SHAPED-CHARGE BOMB[b]

The effectiveness of the warfare waged by Allied planes against German submarines early in World War II was impaired by the difficulty of making hits with single bombs or sticks of bombs dropped in a line pattern and by the defense against underwater blast provided by the saddle-tank construction of the submarines. With the advent of applications of the hollow-charge principle it immediately became of interest to design a small bomb which would defeat the saddle-tank defense system of a submarine by punching a hole all the way through it into the pressure hull. The probability of effective attack would be greater with small bombs because more of them could be carried and more dropped in a single attack.

Late in 1942 the National Defense Research Committee was asked by the Bureau of Ordnance, Navy Department, to undertake the design of a hollow-charge bomb for use against submarines. The bomb was to be the smallest one which would defeat a specified target which would simulate a saddle-tank defense system. It was hoped that the bomb would be small enough to be clustered into groups of 25 to 50 per 500-lb unit.

At the time the request for this bomb was made, studies of the performance of shaped charges under water had not been made, although the Navy Department had conducted a few unsuccessful trials with hollow-charge bombs designed by the U. S. Ordnance Company and loaded at the Eastern Laboratory of the du Pont Company late in 1941. It was therefore necessary for the NDRC to investigate cavity shape, lining material, high explosive filler, charge dimensions, and the like before designing the bomb.

The full-scale target proposed by the Bureau of Ordnance comprised a pair of parallel steel plates with 36 in. of water between them. The first plate, representing the skin or saddle-tank shell, was of $\frac{1}{2}$-in. mild steel. The second plate, representing the pressure hull was of $\frac{7}{8}$-in. high-tensile steel. The bomb was expected to defeat this target in static tests, with the bomb nose in contact with the $\frac{1}{2}$-in. plate, and the bomb axis pitched at an angle of 45° to the planes of the plates. The jet from the bomb was expected to perforate both plates, making a 1- to $1\frac{1}{2}$-in. diameter hole in the 1-in. plate. The actual water-travel distance of the jet, with the plates 36 in. apart, was 48 in. The test was always run with a 50-in. water-travel distance. Since the $\frac{7}{8}$-in. high-tensile steel was difficult to obtain, 1-in. mild steel was generally used as the second plate.

It was necessary to have the stand-off, or free space, between the hollow in the nose of the explosive charge and the end of the bomb nose, as short as possible, and to weight the walls around this space heavily with steel in order to keep the center of gravity of the bomb far enough forward for aerodynamic and hydrodynamic stability. With the stand-off thus limited to about one-half a caliber, the best shape of cavity for deep penetration proved to be a cone of about 45° included apex angle, lined with copper or steel. The preferred method of cone manufacture was by stamping flat sheet of the same thickness as the finished cone, using a series of dies of decreasing bluntness and constant surface area. For experimental purposes a satisfactory method of hand manufacture was developed which did not require dies. Plate of proper thickness was cut to pattern, bent to a conical shape, welded along one seam, and heat-treated.

The smallest bomb which would dependably defeat the target was about 6 in. in diameter, and contained 50/50 Pentolite or 60/40 Cyclotol as filler. Aluminized explosives were evaluated and found to behave as if the aluminum were inert.

The preferred cone, explosive-container shape, etc., were incorporated into the shaped-charge antisubmarine bomb by NDRC, Division 3. Cluster frames, fuze, and scatter mechanism were developed by Division 6 with some assistance from Division 8. A sketch

[b]This section is taken from a report prepared by C. O. Davis. Further data will be found in References 4–10.

of the bomb is shown in Figure 1. The finished bomb had the following characteristics:

Bomb case diameter	6.00 in.
Cone base diameter	5.85 in.
Cone angle	45°
Cone wall thickness	0.185 ± 0.020 in.
Cone material	Mild steel (Armco to SAE 1020)
Cone manufacture	Cold stamping
Explosive	60/40 Cyclotol
Explosive charge length	12 in.
Explosive charge weight	12.5 in.
Bomb length	22 in.
Bomb weight	38 lb

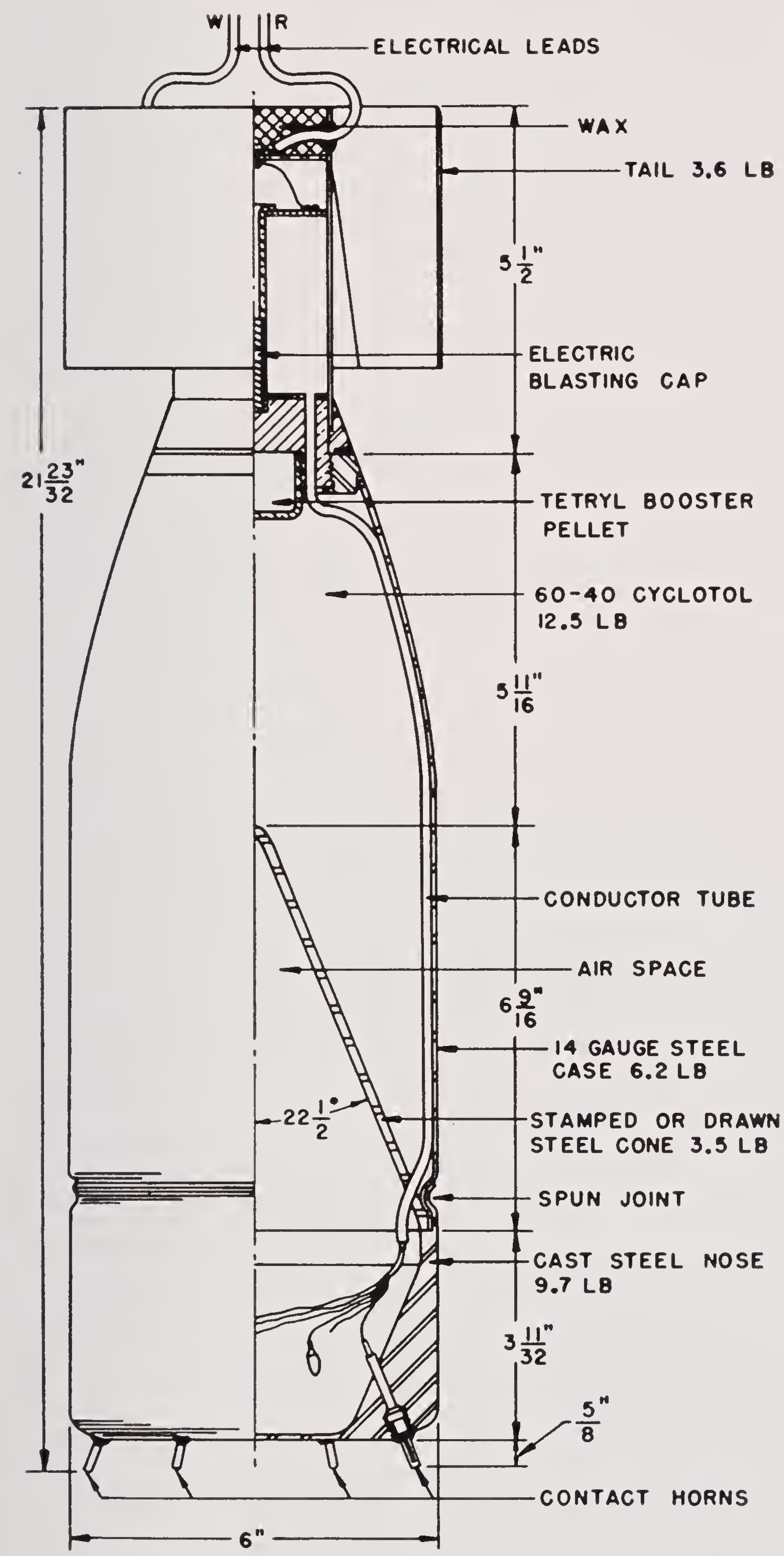


FIGURE 1. Antisubmarine shaped-charge bomb.

This bomb defeated the test target when the latter was wholly in air, partially submerged, or under water at various depths; that is, at conditions simulating a surfaced, diving, and submerged submarine. The hole formed in the 1-in. or pressure-hull plate was a clean, nearly round hole 1 to 1½ in. in diameter with no evidence of cracking or splitting of the target. The bomb gave highly reproducible penetration, and had a small but definite margin of superiority over the target.

Approximately 3,000 bombs were fabricated by NDRC, Division 6, and loaded at Delaware Ordnance Depot, Pedricktown, New Jersey, under the joint auspices of Division 6 and Division 8, for tests by the Navy Department. Delays encountered in the development of first the scatter mechanism and later the fuze prevented use of the bomb in World War II. None of the bombs was ever tested against a submarine.

With no change in shape and little change in weight, the bomb could be improved for attack on the type of target used in the development work by (1) replacing the steel cones by copper cones; (2) replacing the 60/40 Cyclotol by the special high-density 70/30 Cyclotol furnished by the Holston Ordnance Works.

The probable effectiveness of the shaped-charge antisubmarine bomb against the German submarines of World War II is highly conjectural. A statistical analysis of each of the various types of submarines as targets would have to be made to determine the probability of a perforation of the pressure hull on any given hit by a bomb capable of defeating the target used in the development. In the event of a hit resulting in a pressure-hull perforation, one must further know what effect the perforation will have on the operation of the submarine.

It is believed that the shaped-charge design incorporated into the antisubmarine bomb could conveniently and very effectively be carried into bombs of much larger size. Depth of penetration scales approximately in direct proportion to diameter.

3.3 ANTISUBMARINE SHAPED-CHARGE FOLLOW-THROUGH BOMB[c]

The antisubmarine, shaped-charge, follow-through bomb was designed to overcome the limitation in effective range inherent in a hollow-charge weapon

[c]This section is constructed from a report prepared by C. O. Davis.[11,12]

dependent on jet action alone for target damage. Work on the ASCFT bomb was initiated by NDRC, Division 8, when it became evident that the antisubmarine, shaped-charge bomb without a follow-through projectile (described in Section 3.2) would be ineffective in a large proportion of hits on the decking and superstructure of a submarine, where a total penetration greater than the 50 to 60 in. obtainable with the ASC bomb would be required to reach from the plating or decking where the bomb makes contact and explodes through the intervening oil and water to the pressure hull and through the pressure hull. Besides being short in penetration, the ASC bomb would make only a small hole (1- to 1½-in. diameter) in the pressure hull. A shaped-charge bomb with a follow-through projectile, however, would defeat a submarine by putting a hole through the decking or saddle-tank shell through which a high-explosive projectile, carried in the after end of the bomb, would pass. The projectile would be provided with a fuze of long delay to allow it to settle against the pressure hull before detonating. A large hole in the pressure hull would be expected from a fairly small high-explosive charge surrounded by water and in contact with the hull at time of detonation.

At the time the ASCFT research was started, work on hollow-charge devices with follow-through projectiles had progressed far enough both here and in Great Britain so that some features of the assembly, such as design and shape of rear of forward charge to minimize blast effect on the follow-through projectile, were already established. The chief problems to be solved, and their solutions, follow. The weapon itself is shown in Figure 2.

3.3.1 Size and Type of Forward Charge

The most resistant target which the forward charge was expected to defeat was a ½-in. saddle-tank shell with which the bomb nose would be in contact at the instant of detonation. The smallest charge which would dependably open a large hole in a ½-in. plate was 3 lb of Torpex, 3 in. in diameter, having a 45° cone and 1½-in. base diameter, inserted into the rounded nose of the charge. The results obtained with this forward charge indicated that the jet from the cone perforated the ½-in. plate, after which the plate was blown open by blast. The charge without a cone would not hole the plate. Furthermore, when the cone was the full diameter of charge there was no blast damage and the hole was too small for the follow-through projectile.

3.3.2 Design of Follow-through Projectile

A projectile of square cross section was designed because such a projectile in contact with an air-backed 1-in. plate representing the pressure hull, easily de-

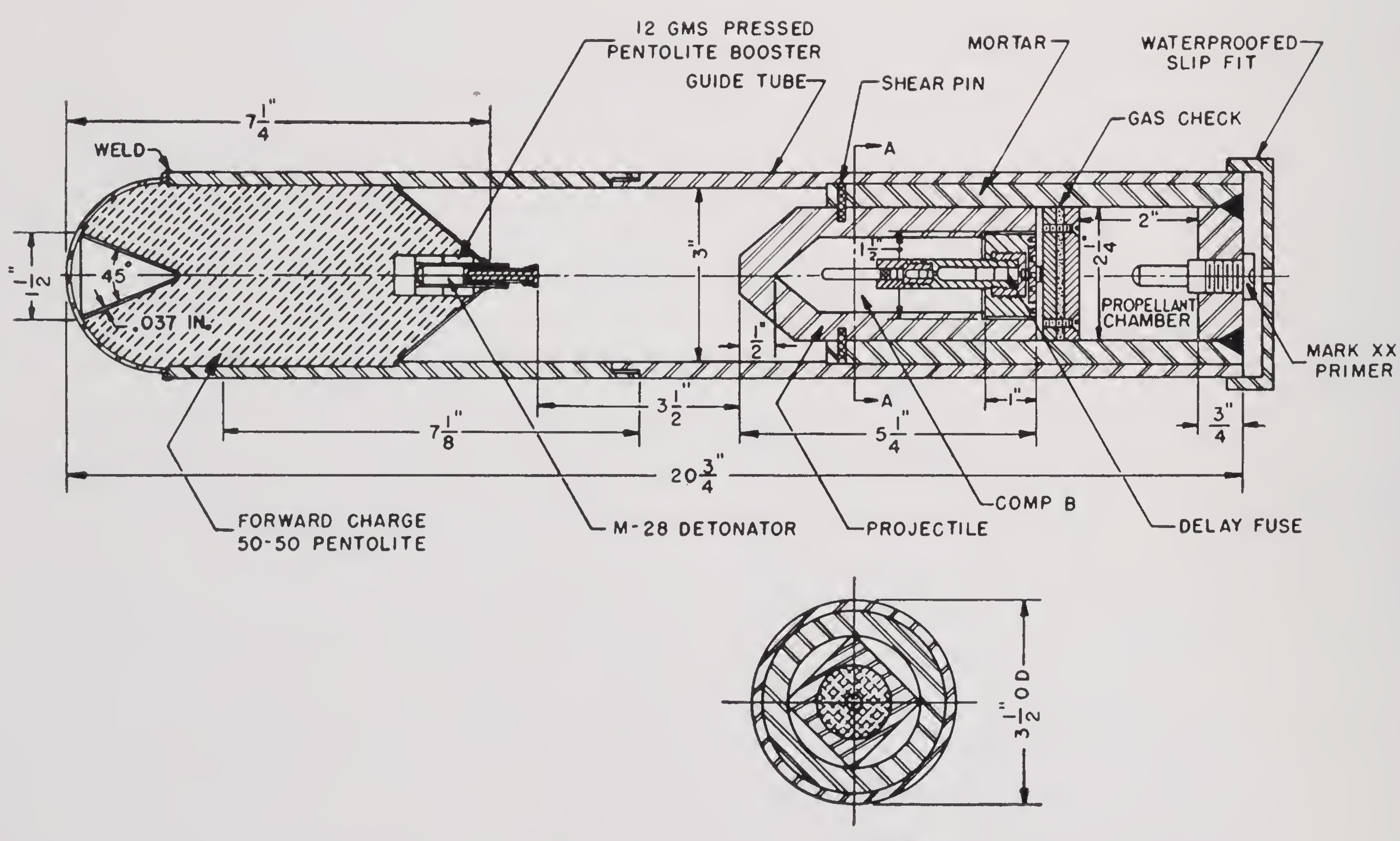


FIGURE 2. Antisubmarine shaped-charge follow-through bomb.

feated the plate when the high-explosive load in the projectile was only 5 oz. of Composition B or the equivalent, whereas a projectile of conventional circular cross section required about 1.5 lb of filler to defeat the target. The preferred projectile of square cross section was 1½ in. wide and 5⅝ in. long.

3.3.3 Propulsion of FT Projectile

The terminal velocity of the ASCFT bomb in water was expected to be only 20 to 30 fps, or too low to cause the follow-through projectile to follow through the forward blast bubble and into the target. A mortar was therefore developed which fired the projectile at the required velocity of approximately 500 fps. The afterend of the projectile carried a special removable gas check, so that the square projectile could be fired from a gun of conventional circular bore. Smokeless powder was used as propellant.

3.3.4 Timing of Explosive Elements

Proper functioning of the various parts of the bomb required the following sequence of actions.

1. Nose of forward charge makes contact with target.
2. Propellent charge is ignited in FT mortar.
3. FT projectile accelerates to full velocity and emerges fully from mortar.
4. Forward charge explodes in contact with target.
5. FT projectile passes through the gas bubble and target, comes to rest, and eventually detonates.

An external fuze was not developed, although a design was proposed by the Ammunition Development Division, Ordnance Department, which would employ a Belleville spring. It was assumed, however, that an external nose fuze would ignite the primer in the FT mortar, perhaps through a Primacord strand, and that the projectile itself would detonate the forward charge by striking an element of a fuze installed at the afterend of the forward charge. All experimental bombs were arranged for firing in this manner. In order to avoid movement of the bomb during the acceleration of the projectile the FT mortar recoiled alone by sliding freely within the bomb body.

3.3.5 FT Projectile

A high-explosive projectile was designed which was not disrupted or deflected by detonation of the forward charge or by passing through the resulting high-pressure gas bubble. A suitable 5-second delay unit was designed at Picatinny Arsenal which, with some modifications, functioned properly.

Successful static tests were run with bombs which were complete except for external fuze, tail, and safety devices. These tests demonstrated the workability of the ASCFT bomb. The using Service with a requirement for such a weapon will be able to start with the design developed under this project but will have to furnish suitable fuzes with safety devices, complete the external design of the bomb including fuze and tail, and develop bundles and clusters of the bombs.

Designs for larger editions of the ASCFT bomb could probably be derived by scaling up the model developed under this project.

3.4 SHAPED-CHARGE WARHEADS FOR NAVAL TORPEDOES[d]

Shaping the charge in the warhead of a naval torpedo to cause deep penetration into a struck ship was among the earliest proposals for military application of shaped charges. A project to develop shaped-charge warheads for Mark 13 (aircraft), Mark 16 (submarine), and Mark 17 (destroyer) torpedoes was authorized late in 1942 by the Bureau of Ordnance primarily with expectation of greatly enhanced incendiary action from such warheads. Early tests with experimental cone-lined charges 6 in. in diameter (between 1/3 and 1/4 scale) showed that the jet from such charges would set fire to combustibles like smokeless powder and oily waste, after penetrating a series of steel plates separated by water, corresponding to the compartmented torpedo defense systems used in American aircraft carriers and various other warships. Subsequent work dealt chiefly with the problem of converting the existing warheads to hollow-charge heads of greatest possible depth of penetration, without changing the external shape of the warhead, or the total weight, center of gravity, and "pull-around" of the torpedo.

As was true with nearly all existing munitions converted from conventional high-explosive to hollow-charge types, the best way to modify a warhead to give deep penetration was to install a small angle (about 45°) steel or copper cone of as large diameter as possible in the forward end of the warhead, with the long axis of the cone coincident with that of the warhead.

[d]This section is taken from a summary prepared by C. O. Davis.[13-15]

Several different compartmented targets, differing in the thickness and spacing of the steel bulkheads and in the location of the air-filled and water-filled compartments, were proposed by the Bureau of Ordnance and the Bureau of Ships in the course of the work and used in full-scale and scaled-down static testing. The two full-scale targets in use by the Navy in tests at Solomon's Island near the end of the project were as follows.

1. Midway Defense System (Full-Scale)

Bulkhead	Skin	1	2	3	4	Safety
Thickness	$\frac{3}{4}$ in.	$\frac{1}{2}$ in.	$\frac{5}{8}$ in.	$1\frac{1}{4}$ in.	$\frac{1}{2}$ in.	
Spacing		5 ft	4 ft	4 ft	4 ft	7 ft
Interplate loading		Water	Water	Air	Air	Air

2. Japanese Defense System (0.304-Scale)

Bulkhead	Skin	1	2	3	4	Safety
Thickness	$\frac{1}{4}$ in.	$\frac{3}{16}$ in.	$\frac{3}{16}$ in.	$\frac{3}{8}$ in.	1 in.	
Spacing		$18\frac{1}{4}$ in.	$14\frac{1}{2}$ in.	$14\frac{1}{2}$ in.	$14\frac{1}{2}$ in.	6 ft
Loading		Air	Water	Water	Air	Air

These defense systems and others were defeated by a modified Mark 13 warhead of the same scale, attacking at 30° from normal, but the other warheads considered for modification were either too short or had such gradually tapered noses that a sufficiently large cone to defeat these defense systems could not be installed in them. Consequently only the hollow-charge Mark 13 or aircraft torpedo warhead was successful, and work on the others was dropped.

Much of the testing to arrive at size and shape of hollow metal lining characteristics, and method of mounting, nose design, charge shape, initiation, explosive composition, etc., was done with charges and targets scaled down to various small scales ($\frac{1}{10}$, $\frac{1}{6}$, $\frac{1}{3}$, etc.) Direct linear scaling was found permissible except for the comparison of certain explosives. Aluminized explosives, such as Torpex II, were inferior to similar explosives without aluminum in small-scale tests but equivalent or superior at larger scale. This phenomenon was observed independently on other projects and by other investigators and was considered due to the failure of the aluminum to react quickly enough to contribute to the detonation pressure in charges below a certain (not definitely established) size.

Aluminized explosives were very much superior to nonaluminized for underwater blast effects (pressure and impulse and target damage), and it was therefore desirable, after adoption by the Navy of Torpex and HBX for Service warheads, to use aluminized fillings in the hollow-charge modification of the Mark 13 warhead. Because of the variation in effectiveness with diameter shown by hollow-charge warheads filled with Torpex and other aluminized explosives, complicated further by large variations in the effectiveness of some of the handmade steel cones used in the test warheads, many series of tests were required before Torpex and a modified HBX (see Section 1.12) were adopted as fillers for the hollow-charge Mark 13 warhead.

The hollow-charge modification of the Mark 13 warhead contained only 520 lb Torpex II, compared with 585 lb for the standard Mark 13, and the general blast damage done to the bulkheads near the outside of the ship would probably be greater with the standard warhead. Sufficient full-scale tests were not made to settle this question. The advantages of the hollow-charge warhead would be in defeating, by perforating and loosening and tearing, the bulkheads beyond the sphere of damage of the standard warhead, in damage to equipment inside the ship, and in superior incendiary effect.

As with other hollow-charge devices, the properties and location of the cone were extremely critical. The Mark 13 warhead required a very large cone ($19\frac{1}{2}$-in. base diameter, $\frac{1}{2}$-in. to $\frac{5}{8}$-in. wall, 45° apex, 100 lb + weight), which was difficult to fabricate. Satisfactory cones were made by the Pittsburgh and Des Moines Steel Company from steel plate of the thickness of the cone wall. Each cone was built from three identical segments, which were cut to pattern and bent to shape. The three seams were welded, the cone heat treated (normalized at 1650 F), and finally trimmed inside and out on a lathe to eliminate eccentricity and variations in thickness or curvature.

Successful full-scale static tests had been made by the Bureau of Ordnance, and a start had been made on designing a hollow-charge Mark 13 warhead for Service use when hostilities ended. An exploder of essentially instantaneous action was required before any firing tests could be made with a Mark 13 torpedo carrying a hollow-charge warhead. Other design work remaining, some of which will require firing tests, was to provide adequate pull-around and strength in the forward end, including the cone mounting to withstand water impact. The firing tests may bring out other structural problems.

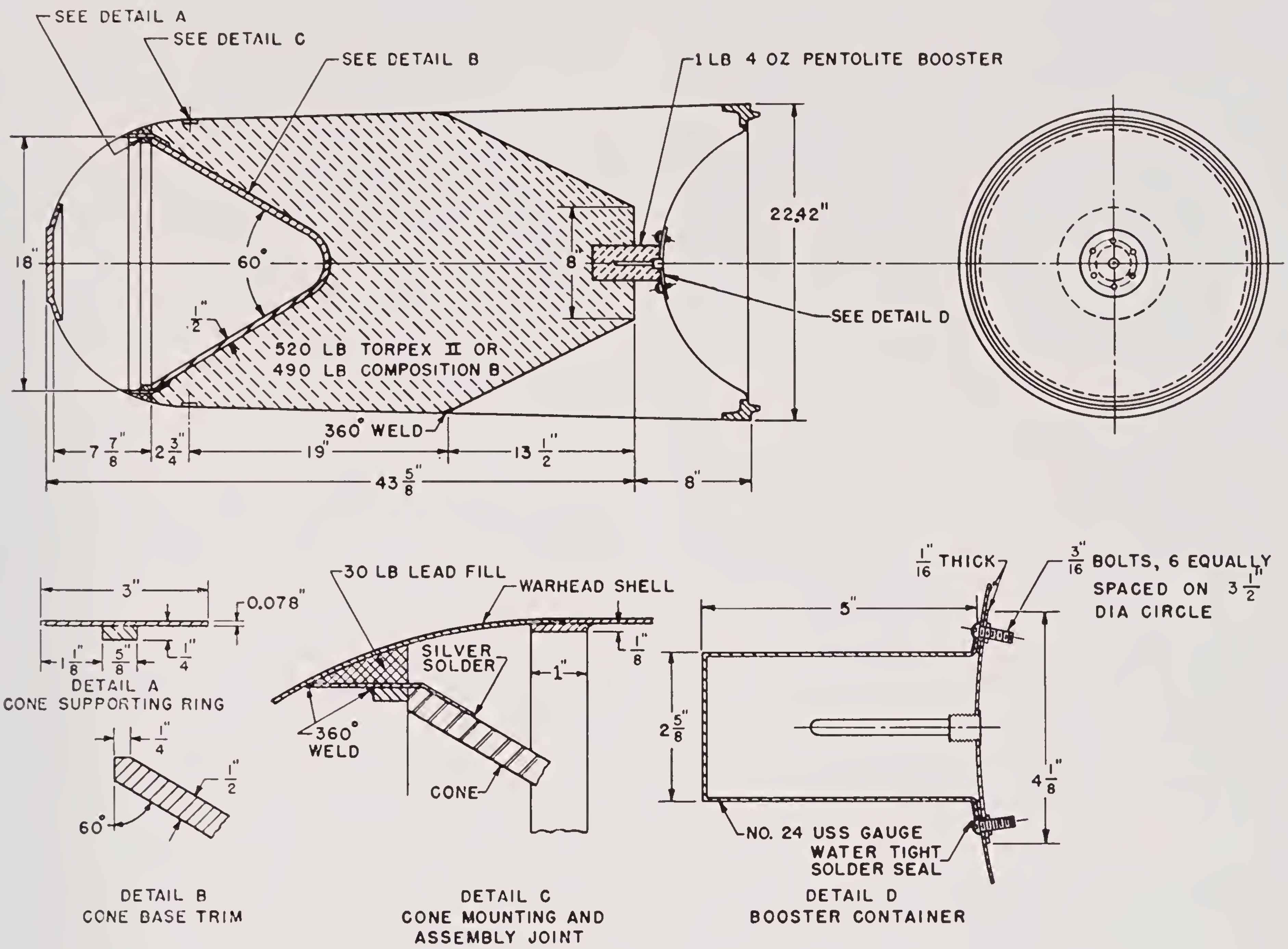


FIGURE 3. Shaped-charge torpedo warhead.

3.5 SHAPED-CHARGE FOLLOW-THROUGH ROCKET[16]

The limitation on a shaped-charge weapon already mentioned in earlier sections of this chapter, that it is capable of doing but little mechanical damage after penetrating the target, led to the request that a shaped-charge projectile with a follow-through device be developed. The final phase of the program had the specific objective of developing a shaped-charge follow-through rocket which would defeat 4 inches of armor plate. The weapon designed to accomplish this was 3½ in. in diameter, weighed 10 lb, and had a velocity of 300 fps utilizing the T-59 rocket motor. The follow-through was an explosive-loaded missile about the size of a 20-mm shell. In the final tests against 4-in. homogeneous armor at normal incidence at 100 yd range, the follow-through passed through the target 12 times in 12 shots and detonated after passage in 10 shots. In comparable trials at 30° incidence, the follow-through passed through the target 10 times in 13 shots and detonated after passage in 7 shots. The brief discussion which follows is limited to a consideration of some of the explosive problems connected with the weapon. For a discussion of propulsion and ballistic features, reference must be made to the Summary Technical Report of NDRC, Division 3, as these features were the responsibility of the Allegany Ballistics Laboratory of Division 3.

In the early work, attempts were made to have the follow-through attached to the apex of the liner of the shaped charge. These attempts were not successful. The slug from the liner parted from the follow-through before the latter had acquired any appreciable velocity. Another problem in the early work was whether the follow-through would be appreciably decelerated by the rearward blast from the shaped charge and in passing through the blast of the shaped charge. It will be recalled that these effects, coupled with the low terminal velocity of the follow-through in the antisubmarine shaped-charge follow-through bomb described in Section 3.4, made it necessary to provide separate propulsion for the follow-through in that weapon. Specific tests, however, made it quite clear that in air the loss in speed of the follow-through was negligible; with 80° conical ends on both the charge

and the follow-through, the loss in speed was not greater than 10 fps.

The principal difficulty encountered in the project was the fuzing. In order to secure detonation of the shaped charge at the rear and on its axis when the shell was at the proper stand-off, a long rodlike striker pin parallel to the axis of the charge was used. This pin struck a detonator back of the charge and initiated the detonation of the charge itself by a connecting piece of Primacord. Later the single striker rod was replaced by three rods located 120° apart. The use of a point detonating fuze was also tried. This fuze, a small shaped charge in the nose of the shell which fires through a flash tube in the main shaped charge by a detonation at its base, was erratic in its action and was eventually abandoned in favor of the rod fuze. The follow-through has a base fuze with a 5-second delay. Although the fuzes functioned satisfactorily in the final tests described in Section 3.5, it is felt that fuzing is the weakest part of the round at present, and further work in the fuzing is recommended before the round is considered for adoption.

3.6 MISCELLANEOUS APPLICATIONS OF SHAPED CHARGES

3.6.1 Destruction of Microwave Tubes

It is desirable to have some means of destroying beyond reconstruction planeborne radar equipment should the plane be forced to land on enemy territory. This can be done by a shaped charge with a liner of sand bonded by a thermosetting resin. The jet from this charge does not have the penetrating power of that from a steel liner, but it does a much better job for this special application. An 80-g shaped charge of either Composition B or 50/50 Pentolite, placed about 3 in. from the target and lined as just described, destroyed the radar oscillator as specified with only small danger to the plane's personnel from blast or fragments; however, the damage to the plane's fuselage was too great to permit use of the device in flight.[17-19]

3.6.2 Shaped-Charge Boosters

A shaped charge is the source of a jet of high intensity, and it is quite natural that the suggestion of using this jet in boosters would arise. The particular problem presented to Division 8 was the use of a shaped-charge booster for the 5-in./38 AA projectile loaded with Explosive D. Tests showed that the standard flat-ended booster was perfectly adequate in this shell, so that nothing was to be gained by going to a shaped charge. The only situation envisaged when the use of a shaped-charge booster would be advantageous would be that where, because of peculiarities of design, the booster was some distance from the main charge.[20]

3.7 BEANO[e]

In August 1943, the Office of Strategic Services requested Division 19 of NDRC to develop a special hand grenade. This grenade, which was given the code name Beano, was to be thrown like a baseball and was, if possible, to be of the same size and weight as a baseball. Preliminary throwing tests, made at the Maryland Research Laboratory of Division 19 with wooden spheres of varying weight but of approximately the same size as a baseball, showed that the weight of these spheres could be increased to 12 ounces without greatly affecting either accuracy or distance. The following specifications were then set for the grenade:

1. It should be spherical and approximately 2⅞ in. in diameter.
2. It should weigh 11 ± 1 ounces.
3. It should be spherically balanced and should not exhibit eccentricity in flight.
4. It should fire as a result of a free fall of 18 in. onto a sponge rubber surface.
5. It should have optimum lethal fragmentation.
6. It should have two arming mechanisms, the initial arming to be reversible and the final arming to take place during flight.

Division 19 took the responsibility for work on the fuze, while Division 8 took responsibility for all problems involving the high-explosive charge. This included not only the selection of the charge, but also the testing for fragment effectiveness and for sensitivity to rifle fire and sympathetic detonation.[f] A contract with the Eastman Kodak Company provided for developing the completed weapon with the assistance of Divisions 8 and 19 and engineering it for possible quantity production.

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[e] This section is based on information supplied by L. H. Farinholt.

[f] The work of Division 8 on Beano has not been described in an OSRD report. This work is to be found, however, in Reference 21 and in Summary Technical Report Division 19, Volume 1, Chapter 4.

Since 12 ounces was the maximum weight allowed and since it was estimated that the fuze assembly would weigh about 2 ounces, there was left 10 ounces for the case and the explosive charge. With both the weight and the dimensions fixed, it was thought that a magnesium or aluminum case might be more effective than a steel case because of the greater wall thickness for a given weight permitted by the light metals. Fragmentation tests, however, showed that a thin-walled steel case was more effective than thick-walled aluminum or magnesium cases of equal weight. Additional fragmentation experiments showed that, for a total weight of explosive and casing fixed at 9 to 10 oz, an 0.040-in. wall steel case was more effective than an 0.060-in. wall steel case of the same diameter. On the basis of these and other fragmentation experiments it was decided to use a spherical steel case, 0.040 in. thick and 2⅞-in. OD, welded at the equator and filled with explosive having a density of about 0.9. With this arrangement the explosive charge and the case each weighed approximately 4.5 ounces.

Some fragmentation tests were made with charges of cast explosives, but, because of the high density of the castings,[g] the permissible amounts of explosive occupied so little space that they created loading problems. Attention was then turned to the following explosives at hand-packing densities: TNT, ammonium picrate, Composition A, and waxed TNT. Granular TNT is probably best from the standpoints of availability and simplicity, but it is somewhat sensitive to .30-caliber rifle fire. Composition A is safe to .30-caliber rifle fire. Grenades loaded with any one of the four named explosives will detonate sympathetically when the grenades are in direct contact with each other. Sympathetic detonation can be prevented, however, by separating the grenades in the container with a layer of cardboard of moderate thickness.

Composition A, granular TNT, and waxed TNT all gave satisfactory fragmentation, while ammonium picrate was decidedly inferior. At a range of 3 ft, a grenade filled with Composition A at a density of approximately 0.9 gave twice as many fragments penetrating a 1-in. pine board as did a similar grenade loaded with granular TNT at a density of 0.8. However, the holes in the board from the Composition A filled case had only half the average area of those from the TNT filled case, so the total area punched out was about the same for the two fillings. The fragments from the Composition A filled case which went through the pine board had an average linear dimension of about 0.23 in.; the comparable fragments from the TNT filled case had an average linear dimension of about 0.31 in. The average velocity of the fragments from a Composition A filled grenade is considerably greater than from the other fillings.

The relative effectiveness at 3 ft and at 10 ft has been determined for TNT loaded and Composition A loaded Beanos. With the TNT charge the number of fragments perforating 1-in. pine board decreases 38% when the target distance is increased from the shorter to the longer distance. With the Composition A charge the corresponding decrease is 50%. However, the number of fragments which go through the pine board is greater at both distances with the Composition A filling.

Comparisons have been made of the fragment effectiveness of the Beano grenade and the standard Mark 2 fragmentation grenade, whose total weight is about twice that of the Beano. At a range of 3 ft, the Mark 2 grenade filled with 2 oz of TNT is about equivalent to a TNT filled Beano but distinctly inferior to a Composition A loaded Beano. The Mark 2 grenade, loaded either with EC powder or granular or flaked TNT, gives no fragments from the quadrant centering around the fuzed end which will penetrate 1-in. pine board at a range of 3 ft. With the Beano grenades the middle third of the quadrant centering around the fuzed end gives a high concentration of effective fragments.

3.8 EXPLOSIVE STREAMERS[h]

In the fall of 1942, Division 8 was requested by the Navy to assist the Naval Ordnance Laboratory with the development of the explosive features of the Holm Antitorpedo Device, later designated the Mark 29 Mine. This device consists of two sets of three streamers, each 400 ft long, which are towed parallel to and at some distance from the two sides of a ship by means of paravanes. The streamers, which must have a slight positive buoyancy, are towed at 10 to 30 ft below the surface. The streamer farthest from the ship on each side contains detecting equipment which signals the approach of a torpedo through the water. The two inner streamers carry an explosive charge, about 1.5 to 2 lb per foot. When a torpedo passes under the detector streamer, the outer explosive streamer is de-

[g]Cast 50/50 Pentolite, for example, has a density of from 1.59 to 1.65.

[h]This section is constructed from reports furnished by D. P. MacDougall and C. O. Davis.[22-24]

tonated after a slight delay, so that the torpedo is destroyed or at least prevented from reaching the ship. Should a second torpedo later approach the ship from the same side, it is dealt with in a similar way by the other explosive streamer.

The first form of explosive streamer, or hose, developed by the Naval Ordnance Laboratory consisted of a large rubber hose partly filled by cans, 2 in. in diameter and 8 in. long, of Nitramon-S primer, an amatol-like explosive. Primacord was used to insure propagation from can to can. This hose had a number of disadvantages, the chief ones being that it was very time-consuming to load and that detonation of one of the explosive hoses compressed the explosive in the adjacent hose sufficiently to prevent it from propagating detonation when called upon to do so.

A suitable design of explosive streamer had to meet a number of conditions: ease of manufacture in large quantities; flexibility (the filled hose had to be able to be wound on a 3-ft reel); ability to stand countermining and rough handling; reliability of propagation; and suitable buoyancy.

Two organizations were chosen to work on the NDRC phases of this development, the Eastern Laboratory of the du Pont Company and the Explosives Research Laboratory at Bruceton. Each group considered both discrete charges and continuous, long charges for the filling, but the major developments made by both groups, although somewhat different, involved rather long, flexible inner hoses filled with explosive. The development at the Explosives Research Laboratory will be described first, and will be followed by a description of the developments at the du Pont Eastern Laboratory.

At the time work was begun, the only explosives available in sufficient quantity were TNT and, possibly, Pentolite. Because of the requirement that the streamer have slight positive buoyancy, and because the densities of all the hose materials and metal couplings are considerably over one, it seemed impossible to avoid using the Naval Ordnance Laboratory scheme of providing buoyancy by using for the outer container a hose partly filled with explosive and partly filled with air under pressure. No practical way was found for filling the outer hose completely with explosive material having a density considerably less than one. An inner hose filled with cast TNT would have been simple to produce, but it would not have met the flexibility requirement nor would it have propagated reliably. Cast Pentolite would have propagated satisfactorily but it would not have been flexible and it might have been too sensitive.

It was discovered at the Explosives Research Laboratory that, if a hose is filled with molten TNT and then flexed gently during the cooling period, the resulting charge consists of finely divided TNT at a density of about 1.40 g per cc. Because the TNT is powdered, the filled hose is fairly flexible, meeting the requirement easily, and the charge propagates reliably. (Pressed crystalline TNT propagates detonation reliably under conditions of diameter and confinement for which cast TNT will usually fail to propagate.)

The first mechanical device for carrying out this flexing operation was built and operated at Bruceton, but for larger scale studies a group from the Explosives Research Laboratory went to the Naval Mine Depot, Yorktown, Virginia. The first flexing machine involved reciprocating arms and gave the filled hose a rather snake-like motion while cooling; later it was found that a more gentle treatment would be adequate, and the final flexing machine consisted of a pair of large drums, 4 ft in diameter with 1-ft face, spaced 7 ft apart and connected by a continuous belt. Twenty-five-foot lengths of hose, filled with molten TNT and plugged, were wrapped around the two drums and the ends fastened. The machine was run for about 50 minutes, after which the hose was found to be almost completely filled with fine-grained TNT, with only an inch or less of hard material at the ends. Several sizes and varieties of hose were successfully loaded and flexed, but for the specified load of 1.5 lb per foot, hose with 1.75-in. ID, was suitable. Some 2,400 ft of hose were loaded and flexed with the two-pulley machine described above. The capacity of this machine was four 25-ft lengths per hour. By increasing the width of the pulley faces to 3 or 4 ft, the output could be stepped up considerably with little increase in space requirements.

In addition to developing the flexed TNT-filled inner hose, suitable outer hose and couplings were designed and procured. The completely assembled streamers were tested for propagation and countermining. The propagation tests were completely successful in 400-ft lengths, but the streamers stood up only moderately well to the detonation of a similar streamer near by. This was a fault of the outer hose and could have been remedied. However, due to changing requirements, this type of streamer was never actually used in service in the Mark 22 Mine. Interest

was aroused in the possibilities of using the inner hose as a demolition charge. A somewhat larger hose was used in order to increase the weight of explosive per foot, and it was given the designation of the Mark 8 demolition charge. On the basis of the work carried out for the Mark 29 hose, Explosives Research Laboratory personnel cooperated with Navy personnel in the design of a plant for producing this flexible explosive hose. A plant was built at Yorktown to this design, and was operated for some time at a rate understood to have produced about a million pounds a month of explosive hose.

The Eastern Laboratory of the du Pont Company developed a 50/50 mixture of grained and flaked TNT which could be poured into the canvas inner tube to the same loading density as was attained with grained TNT by vigorous hand tamping. This simplified and speeded up the loading. The improved TNT canvas-sock load was used in all of the Service tests and actual applications of the Mark 29 device, although the explosive streamers containing this load were objectionable for the following reasons.

1. Primacord was needed to insure propagation. The Primacord was bullet sensitive, easily desensitized by water, and tended to cut off during detonation at places where it was looped or bent.

2. Loose TNT was not particularly waterproof, fire- or bulletproof.

3. The streamer had an undesirably large amount of metal in it as couplings between 25-ft lengths. This made more difficult the attainment of buoyancy and cut down on flexibility. A single continuous column of explosive appeared desirable in place of 25-ft lengths.

4. The use of compressed air for buoyancy required special extra-heavy hose to contain the explosive and air and introduced various complications in the handling and storage of the streamers. Rubber was very scarce, and large quantities were required.

A load consisting of pressed, round-ended pellets of TNT, strung like beads on Primacord, was first proposed to replace sock loading. The pellets could be pressed at an Army Ordnance Works and shipped to the Mark 29 assembly plant where assembly into the buoyancy hoses would be very easy and rapid. This type of load was unsuccessful, however, in countermining tests. The pellets developed dust, and some breakage occurred.

A series of slurry-type explosives was developed which could be poured or pumped into continuous tubes of various sizes down to 1 in. in diameter. The two preferred compositions and their properties are given below.

	Composition EL-387A	Composition EL-387B
50/50 Pentolite	30.0%	24.0%
Ammonium nitrate	54.0%	43.2%
Water	13.5%	10.8%
Starch	2.5%	2.0%
Aluminum (MD101)	None	20.0%
Density of filling	1.33–1.40	1.50
Triton value	10.9	13.4
TNT equivalent, from underwater blast measurements	0.856-lb TNT/lb	1.207-lb TNT/lb
Propagation	OK in 1 in.x50 ft	OK in 1 in.x50 ft
Sensitiveness		
Air gap	12 in. in $1\frac{3}{4}$ in. diam 2 in. in 1-in. diam	11 in. in $1\frac{3}{4}$-in. diam 0 in. in 1-in. diam
Water gap	4 in. in $1\frac{3}{4}$-in. diam $\frac{1}{2}$-in. in 1-in. diam	4 in. in $1\frac{3}{4}$-in. diam 0 in. in 1-in. diam
Cap sensitivity		
Eng. Spec. No. 8	Detonated	Detonated
No. 6 EBC		Failed
Thermal stability	Brown fumes at 150C* Ignited at 170 to 180C*	Brown fumes at 150C* Ignited at 170 to 180C*

*Same as 50/50 Pentolite.

Pentolite was used as the sensitizer for the explosive slurry because it detonates dependably in water. Ammonium nitrate was used as a source of strength and also because its solubility in water increases very rapidly as the temperature is raised. Both EL-387A and B were mixed and poured at 60 to 70 C, or just below the melting point of the Pentolite. On cooling to room temperature both slurries stiffened due to crystallization of ammonium nitrate. The resulting column of explosive was flexible down to —30 C, but sufficiently solid so that settling of solid ingredients did not occur. Seepage of liquid was avoided at room temperature and above by addition of a small amount of starch.

The water-slurry compositions were satisfactory as regards propagation, strength, stability, and failure to be exploded by rifle bullets. Hoses loaded with them withstood rough handling tests by Naval Ordnance Laboratory and were flexible and easily manipulated.

Some uncertainty existed throughout the Mark 29 project concerning the weight of explosives to use per foot of streamer. It was desirable to keep the weight at the minimum which would destroy torpedos at a reasonable maximum distance of 20 ft. Larger charges than the bare minimum had to be avoided to keep at a minimum the damage done by the exploding streamer to the ship it was protecting, and the damage

to the audio-detector streamer. The TNT sock load was 1.6 lb per foot, and the experimental streamers were loaded to a TNT equivalent (based on Triton value) of 1.6 lb per foot. Tests by the Naval Ordnance Laboratory toward the end of the project indicated that a charge weight of 1.0 to 1.2 lb of TNT per foot might be adequate.

Explosive streamers loaded with EL-387A and B were unsatisfactory only with respect to overall density, which was 1.35-1.50 g per cc. The overall density of a Mark 29 streamer had to be approximately 1.04 g per cc for proper buoyancy. Unsuccessful attempts were made to obtain this buoyancy by bringing the slurry density down by the addition of buoyant diluents and by the use of various floats within or around the streamer. Finely divided material within the explosive interfered with propagation and strength, and large pieces of buoyant material failed to withstand countermining. It was necessary to retain the Naval Ordnance Laboratory method of regulating buoyancy with compressed air.

The production of Mark 29 units by the Navy was discontinued before any streamers developed by NDRC had received complete field tests.

Nonbuoyant streamers loaded with EL-387A or B would be useful line-demolition charges, particularly for underwater demolitions. EL-387A and B would be particularly well suited for use as "drone" charges, where it is desired to load or pour the maximum weight of explosive in minimum time in a boat or similar carrier of any size or shape which is to be run up to the firing point by remote control and detonated en masse.

3.9 LIQUID EXPLOSIVES[i]

At the request of the Army Corps of Engineers, under Service Project CE-32, Division 8 was asked to develop a liquid explosive for use in mine clearing. The Division was also requested to furnish help and advice on the design and construction of a device for dispensing a liquid explosive in the field into a flexible hose. The hose itself was to be laid in the mine field by means of a rocket and upon detonation was expected to clear a safe path for tanks and for personnel. It was the responsibility of Division 8 to develop the explosive, and it was the responsibility of the Corps of Engineers to evaluate its mine-clearing efficiency. Results on standard minefields are reported by the Engineer Board, Ft. Belvoir, Virginia, and will not be discussed here.

[i]This section is taken from a summary prepared by Howard J. Fisher.[25,26]

The requirements for the liquid explosive were as follows:

1. It should be safe to handle both during manufacture and transport.
2. It should be as insensitive as possible to enemy small arms fire.
3. It should propagate a high-order detonation in diameters as low as 1 in. in the unconfined state. This requirement was later altered to permit propagation in diameters only as low as 3 in. because a larger hose carrying a minimum of 4.5 lb of explosive per foot was expected to be used against antitank mines.
4. It should be capable of being stored in the usual Service magazines.
5. It should have a low freezing point to avoid crystallization in the field.

The development of liquid explosives was carried out at the Explosives Research Laboratory, Bruceton, Pennsylvania, under Contract OEMsr-202 and at the Eastern Laboratory of the du Pont Company, Gibbstown, New Jersey, under Contract OEMsr-828. Tests were conducted at the Engineer Board Field Station, Port Royal, Virginia.

Four liquid explosives were developed. All were based on a 75/25 nitroglycerin-nitroglycol mixture (No. 8 oil) because it is the only liquid explosive manufactured in this country in sufficient quantities for wartime use. The nitroglycol was used to lower the freezing point of the nitroglycerin.

Two compositions based on nitroglycerin desensitized with dimethyl phthalate and stabilized with ethyl centralite were developed at ERL. Two other compositions based on nitroglycerin desensitized with a 70/30 mixture of DNT oil-TNT and stabilized with diphenylamine were developed by the du Pont Company. The exact formulations follow.

Methylite 20		Methylite 25	
Nitroglycerin-nitroglycol (75/25)	80	Nitroglycerin-nitroglycol (75/25)	75
Dimethyl phthalate	20	Dimethyl phthalate	25
Ethyl centralite	0.8	Ethyl centralite	0.75
EL-389 A		EL-389 B	
Nitroglycerin-nitroglycol (75/25)	55	Nitroglycerin-nitroglycol (75/25)	60
DNT oil-TNT (70/30)	45	DNT oil-TNT (70/30)	40
Diphenylamine	0.55	Diphenylamine	0.6

Considerable time was devoted to a study of the sensitivity of these liquids in a number of impact machines. Depending upon the conditions of confine-

ment and upon the types of strikers and anvils used, the sensitivity of all the liquids ranged between that of dry PETN and crystalline TNT. In all cases they were shown to be considerably less sensitive than nitroglycerin. Furthermore, they were found to be insensitive to frictional impact and did not detonate in any friction device tried.

Methylite 20 and 25 and EL-389B and A were also found to be insensitive to .30- and .50-caliber ball and tracer ammunition when backed by air and confined in 1- and 3-in. diameter neoprene-impregnated Fiberglas hose. They gave fires approximately half the time when struck by .30 caliber incendiary ammunition and gave detonations when fired upon with .50 caliber incendiary ammunition.

The four liquid explosives studied were, in a limited number of tests, insensitive to .30 caliber ball and tracer ammunition when contained in thin steel containers (such as Jerricans or Army Air Forces gasoline cans) or when held in light-walled aluminum containers which were rubber lined. They are probably sensitive to incendiary ammunition in both the lined and unlined containers.

In order to satisfy Navy shipping requirements, a number of drop tests were made. In the first series of tests these liquids were shown to be insensitive to drops of 50 ft onto armor plate supported by packed earth when contained in Army Air Forces gasoline cans and packed for shipping in boxes of ¾-in. wood having about 1 in. of sawdust between the wood and the container. Ten drops were made with each explosive.

Another series of drop tests was made under the following conditions at the request of the Bureau of Ordnance. A special shipping container developed by the packaging section of Picatinny Arsenal specifically for these liquids was dropped from a height of 50 ft onto armor plate studded with railroad spikes arranged so that at each drop at least one spike penetrated the container.

The Picatinny containers are 10-in. cubes made of thin copper covered on the outside with ⅜-in. plywood held in place by a mortised joint which runs along each edge of the cube. The top cubical face contains a large hole near the center for filling and emptying. The closure for this hole consists of a neoprene-gasketed lid held in place by a spider. Two of these containers, each holding 2½ gallons (30 lb of explosive) are packed in a box similar to a standard ammunition box and having approximate dimensions: 26-in. inside length, 14-in. inside width and depth. This box is made of ¾-in. wood with reinforcement at the ends. The two inner cubical containers are spaced with Celotex and cardboard so that they are about 2 in. from each other and from each inner face of the ammunition box.

In ten drops each with Methylite 25 and EL-389A there were no detonations. In every drop the spikes penetrated the containers and liquid was spilled onto the armor plate.

Two devices were designed for dispensing these liquid explosives in the field. They were built by the M. W. Kellogg Company, Jersey City, New Jersey, under an Engineer Board contract. A representative of Division 8 from the Explosives Research Laboratory and from the du Pont Company approved and selected valves, connections, and closures for the tanks. In all cases where contact with the liquid explosive was expected, the moving parts were arranged so that no metal-to-metal contact was possible between surfaces which were wet with liquid explosive. The first prototype, known as the Dragon No. 1, was built to hold 2,250 lb of liquid explosive. The tanks were installed in a M10A1 3-in. gun carrier. The liquid was forced from the tank through a rubber-lined valve into a 500-ft length of 3-in. neoprene-impregnated Fiberglas hose which was launched by a rocket. It was possible to dispense the 2,250 lb of explosive in 1½ minutes under air pressure of 70 psi.

The second device, known as the Dragon No. 2, was arranged for holding 4,500 lb of liquid explosive in three tanks connected in series. The containers were completely enclosed in a T4 25-ton tank. Space was also left for a driver, an assistant driver and an explosive operator. In this design the liquid was forced into three 150-ft hoses 3 in. in diameter launched by a rocket-and-yoke mechanism so that the three hoses fell in a lane no wider than 15 ft. This arrangement was necessary because it was shown by tests that a single linear charge did not clear an adequate path for tanks through the quite insensitive Japanese land mines. It was expected from static tests with hand-laid hoses that three hoses lying symmetrically in a 15-ft lane would clear an adequate tank path.

Boosters which will initiate high-order detonation at a velocity of 6,800 to 7,400 mps in these liquids may be made of cast Pentolite or Composition C-2 arranged in a cylinder, 5-in. OD by 3-in. ID by 6 in. long, placed around the hose or, more simply, by shooting small shaped charges axially or diametrically into the hose.

Valve, tank linings, and hose materials may be

made of neoprene, compounded GRS, Vinylite, Butacite, or Koroseal. Neoprene and compounded GRS are probably the best. Hycar, noncompounded GRS and Resistoflex are not satisfactory.

Briefly summarized, the problem stands as follows. Four liquid explosives have been developed. These are based on commercially available materials, have withstood one month's storage at 71 C (160 F), and have been stored for two years at ordinary temperatures without apparent deterioration. They are insensitive to .30 and .50 caliber ball and incendiary ammunition when unconfined. They are not detonated, when properly packaged, by drops of 50 ft onto spike-studded armor plate. Being of reasonably low viscosity (about 80 centipoises at 0 C) and of reasonably low freezing point (about −10 C), they may be dispensed at temperatures usually encountered in the field into flexible hoses 3 in. in diameter at the rate of about one ton in 90 seconds by air at a pressure of 80 psi.

3.10 INCREASED VISIBILITY OF AA SHELL BURSTS

An early request made of Division 8 was to devise a method of increasing the visibility of the bursts of antiaircraft shell. A quantitative photographic method was employed to measure the brightness of bursts of ⅓ (weight) scale models of 3-in. AA shell. The standard loading of the model shells was 150 g of cast TNT plus a 20-g tetryl booster. When 15 g increments of the following materials were added the ratio of the brightness of the burst to that of the standard loading was

Red phosphorus	15
Silicon	50
Aluminum	400

The silicon and aluminum should be placed in a small container at the base of the shell in order to be most effective. With the aluminum, variations in particle size between 20 and 250 mesh were without effect. Aluminum also increases the duration of the flash from about 2.5 to about 17 milliseconds. The original reports show the improvement in visibility attained by using less than 15-g increments; this permits the calculation of the amount of additive required to produce a given visibility. Tests with other additives, less effective than the three listed above, are also reported.[27,28]

Chapter 4

EXPERIMENTAL STUDIES OF EXPLOSIVE PHENOMENA

This chapter will deal almost entirely with studies of shaped charges,[a] but that discussion is preceded by a very brief mention of the flash photographic technique and its application to explosive phenomena and by a summary of studies of shell fragmentation.

4.1 FLASH PHOTOGRAPHY

When a solid sphere of high explosive, for example 50/50 Pentolite, surrounded by argon, is detonated at its center, the resultant shock wave in the argon produces a flash of light of high intensity and short duration. (Under favorable circumstances durations of 0.5 microsecond have been obtained). The intensity of the flash is roughly proportional to the spherical surface of the explosive, its duration to the thickness of the gas layer.[1] The light flash enables explosive phenomena to be studied photographically.

Two extensions of the technique have considerably enhanced its utility.[2]

The first consists of the use of a high-speed shutter which permits reflection photographs to be made of, for example, expanding shell cases without interference and fogging from the relatively long duration shock wave and combustion luminosity of the detonation products. When simple shadow pictures are made, it is possible to use a small enough camera lens opening to prevent interference by the relatively low-intensity after-light. When reflection pictures are made, however, the subject light intensity is much lower, and in order to prevent the after-light from fogging the picture, the camera must be closed in a time of the order of microseconds after the detonation of the flash bulb.

A simple and effective shutter was devised by passing the ends of two pieces of Primacord in front of and about an inch away from the heavy glass protective window, just above and below the field of view of the camera. The Primacord fuzes are of such length that they detonate several microseconds after the flash bulb. The opaque products from the Primacord expand in front of the camera lens and effectively close it. The shutter remains closed because of the formation of a layer of soot and carbon on the heavy glass window. The detonating fuze next to the window is covered with a layer of vaseline and carbon black to increase its effectiveness for this purpose.

A second extension of the flash photography technique is concerned with the development of a relatively long-duration light source for use in conjunction with the drum or mirror camera to obtain rate pictures of rapidly moving nonluminous phenomena—water shock waves, for example. To produce the intense light of 40 to 50 microseconds duration necessary for this purpose, the light bulb is made in the form of a transparent tube filled with argon with an explosive pellet at one end of the tube. (An earlier form of the light had a narrow column of explosive at the axis of the tube.)

The flash photographic method has been applied to a variety of explosive phenomena, for example, the formation of jets from cavity charges and the qualitative and quantitative aspect of expanding shell cases. These and other applications are described in detail in the reports already cited.

Shock waves in air and in water were investigated, using both the rotating drum camera[3] and flash photography. The data obtained have been presented in a formal report.[4] The principal interest in the work lies in the fact that quantitative observations were made of much more intense shock waves (shock-wave pressures of the order of hundreds of atmospheres in air) than are customarily studied by other means.

4.2 STUDIES OF SHELL FRAGMENTATION

In order to study and compare the effectiveness of various shells or bomb casings and fillers, it is necessary that data be available on (1) the average fragment velocity and the fragment velocity distribution at various directions with respect to the shell axis; (2) the mass and size distribution of the fragments, also as a function of direction from the shell; (3) the retardation coefficient for the fragments, i.e., the rate at which their velocity decreases due to air resistance; and (4) standard target damage data for fragments of various sizes and velocities. If sufficiently accurate and detailed data of this kind are

[a]The discussion of shaped charges is from a summary prepared by M. A. Paul. The discussion of the remaining items in this chapter is based on information supplied by G. H. Messerly.

available, it is possible to make reliable predictions of the effectiveness of shells against various kinds of targets and at different target distances. The program of study at the Explosives Research Laboratory [ERL] was designed to supply such data.

The method of fragment velocity measurement developed at the ERL measures the velocities of a number of fragments from a single burst whose trajectories are defined only within a known solid angle. It consisted of recording, with a rotating drum camera, the shadow images of the fragments passing between the camera and three illuminated slits. The three image spots produced by each of a number of fragments passing in front of the camera at about the same time are easily identified, and the fragment velocity is deduced from their spacing on the film.[5]

The individual fragment velocities were measured with an error of about ± 2%. The velocity measurement was made over a distance of 2 ft at an average distance of 8½ ft from the shell. After passing in front of the camera, the representative group of fragments were received on a target which recorded their penetrative power. If this target was made of wood, telephone books, or other suitable material, the individual fragments were preserved and identified with the measured velocities. The method thus gave, for each fragment of a representative group from a bomb or shell burst, a measurement of the mass and velocity; and, depending on the amount of distortion which the fragment suffered when it is stopped, the fragment size and shape. Further, from the change in appearance of the image spots from one slit to the next, it was possible to make a rough estimate of the rotational velocity of the fragment.

The shell to be studied was detonated in the center of a 20x20-ft chamber, with the shell axis vertical and the center of the shell about 2 ft from the floor. A band of fragments 15 degrees in width and from 1 to 2 ft high was used for the velocity measurements. Penetration and fragment distribution measurements were made at the same time on a large portion of the side wall band of fragments by means of targets placed around the sides of the room. From a single burst it was thus possible in principle to obtain complete information on the fragmentation of a given shell. Because of the spread in fragment velocity, however, it is usually necessary to fire about six shells to obtain a statistically significant average velocity value.

As indicated above, in order to predict the useful range of the fragments, something must be known of their deceleration from air resistance. To provide such data, the single-station apparatus described above was expanded to allow velocity measurements to be made at three distances, 9¼, 25½, and 78 ft from the shell. The experimental arrangement for these measurements, and the results obtained are described in reference 6.

Some data on the size distribution of the fragments may be inferred from the distribution of hit sizes on the steel target panels, and a smaller number of data on the actual fragments were obtained from the fragments recovered from the wood targets. It is much more efficient, however, to obtain the mass and size distribution of the fragments from pit firing in which all the fragments from a given shell are received in sand or sawdust and recovered therefrom.[7-9]

From the foregoing it seems that in principle, at least, all the requisite data for the evaluation of a shell may be obtained. The actual results, however, summarized below, are far from complete and constitute only a beginning in the study of this subject.

In a study whose main purpose was the determination of the effect of casing thickness on the fragment velocity and penetration, simulated shells of 2-in. ID and wall thickness of ⅛, 3⁄16, 5⁄16, ⅜, ½, and ⅝ in., filled with TNT, Ednatol, Cyclotol, and Torpex, were studied. In addition a number of other explosives were studied in ½-in. thick cases. It was found[10] that the average fragment[b] velocity was a nearly linear function of $(\text{charge weight/casing weight})^{0.58}$ a conclusion later confirmed over a wide range of charge ratio by flash photography studies.[2]

The relatively small amount of data on fragment retardation may be summarized.

1. The maximum or mean fragment presentation area per unit mass of fragment does not seem to be a very useful criterion for predicting fragment retardation. (This remark applies only to fragments of the indicated size and velocity range and over a disstance range of 27 ft from the shell. Studies with smaller fragments and/or larger distances would undoubtedly show some dependence, and research in this direction should certainly be undertaken.)

2. About ⅓ of the fragments studied exhibited appreciable rotation, while ⅔ were stably oriented. This fact suggests that it is not very useful to apply to the problem of fragment retardation a mathematical analysis which postulates random orientation of a given fragment with respect to its direction of flight.[12]

The relative effectiveness of different explosives in

[b] Controlled fragmentation of thin-walled casings is discussed in Reference 11.

the same casing was examined for Ednatol, 55/45 TNT/Aluminum, Cyclotol, HBX, PTX-1, PTX-2, TNT-D2 95/5, Tritonal-D2 95/5, Picrotol 52/48, Pipe, Torpex II, Pentolite, Composition A-3 91/9, Composition A 88/12, Amatol 80/20, and TNT. The last-named explosive was used as a control. Maximum average fragment velocity differences of about 25% were found among the various explosives. The differences in average velocity showed in most cases a fair correlation with the number of fragments of various degrees of effectiveness and with the ballistic mortar value for the explosive in question.[13]

In an attempt to place the data for target damage on a more systematic basis, an attempt was made to determine, for several velocities and target thicknesses, the smallest fragment mass which will just perforate, and the largest mass which will just fail to perforate a given target. The results of voluminous target penetration data bearing on this problem have been collected together with frequently useful formulas relating the fragment momentum per unit area to the penetration in targets of wood, paper (telephone directories), and steel, and the average mass and area of shell fragments.[14]

Both the single and the multiple station velocity apparatus were used to compare the effectiveness of explosives in various types of actual shells.[15-25]

A target damage study program was made with the objective of determining the optimum wall thickness of mortar shells designed for use with proximity fuzes.[26] The experimental setup used for these static firing tests consisted of two 9-ft high semicircular target "fences" of 1-in. thick yellow pine. One of the semicircular target fences was of 20-ft radius; the other of 40-ft radius. The shell was hung at the common center of the semicircular targets, with the shell axis horizontal, and in line with the common diameter of the semicircles so that equivalent fragments were received on both targets. This work was necessarily done in a proving ground area.

The significant results of the investigation may be summarized:

1. There is little difference in effectiveness or appreciable shift of fragment distribution with change in wall thickness of 0.050, 0.060, 0.080, 0.090, and 0.110 in.

2. Change from nose to tail imitation shifts the peak in fragment distribution from about 100 to 80° (nose = 0°).

3. Composition B is 10 to 15% more effective than TNT.

4.3 SHAPED CHARGES

4.3.1 Introduction

The discovery of the shaped charge or cavity effect is generally attributed to C. E. Munroe, a civilian chemist working for the U. S. Navy at the time. In several papers published during the period from 1885 to 1900 he showed that a cavity hollowed in the base of an explosive charge resulted in a deep hole instead of the usual shallow depression in a steel plate on which the charge had been standing. The phenomenon was reinvestigated in Germany in 1914 by E. Neumann, who studied the effect of varying the cavity shape and observed that penetration persisted when the charge was removed a short distance from the target. No use, however, was made of shaped-charge weapons during World War I.

The basis of modern shaped-charge developments is the introduction by H. Mohaupt in 1937 of a metal liner in the cavity. With a suitable metal liner, the depth of the hole in the target may be increased more than threefold over that produced by an unlined cavity charge. Furthermore, the lined charge is effective at a considerably greater distance from the target; for the conventional liners now in use, a stand-off of several charge diameters is required to attain maximum depth of penetration.[c]

Shaped-charge weapons have been extensively used in World War II by all major armed forces. Research on shaped charges in this country, particularly on the part of the National Defense Research Committee was stimulated by pioneer work in Great Britain to which we are deeply indebted.[d]

American shaped-charge weapons that have been in Service use include the M9A1 rifle grenade, the spectacularly successful M6A3 2.36-in. HEAT rocket (the Bazooka), the M307 HEAT shell for the 57-mm recoilless gun, the M66 and M67 HEAT shell for the 75-mm and 105-mm howitzers, and several Engineers' demolition charges. Weapons in various stages of development, but not completed in time to be applied by the Armed Services include a shaped-charge torpedo warhead, a HEAT round for the 4.2-in. recoilless chemical mortar, shaped-charge bombs of various sizes, a high-velocity 2.36-in. HEAT rocket, and several other projectiles of different sizes.

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[c]The early developments are described in reference 27.

[d]Excellent reviews of British work are to be found in references 28 (a review to the end of 1942); 29 (the early part of 1943); 30 (the period from August 1943 to August 1944); and 31 (this includes ARD Explosives Report 669/44).

Division 8 sponsored the development of several specific shaped-charge weapons, described in Chapter 3.

Fundamental research on shaped charges by Division 8 was carried on at the Explosives Research Laboratory, Bruceton, Pennsylvania, which also participated directly in certain specific shaped-charge weapon developments.

In the general description of shaped-charge phenomena that follows, we have borrowed freely from British sources of information and also from work in this country carried on at the Eastern Laboratory of the du Pont Company under contract with the Army Ordnance Department, and at the Ballistic Research Laboratory, Aberdeen Proving Gronnd, Maryland. The present state of our knowledge has been derived from many sources and we do not pretend in this summary report to have assigned full credit to all the various organizations and individuals who have contributed to this knowledge.

4.3.2 General Properties of Cavity Charges Fired in Air

Cavity charges fired against steel or concrete targets in air produce, typically, holes several calibers deep and rather small in diameter in the target. If they fail to perforate the target, no special damage is done on the other side. If they do perforate the target, they will disintegrate objects directly in the line of fire, that is, along the extended charge axis. Further damage may be done by spalled material from the rear of the target, but such damage is generally confined to a region of perhaps 20° solid angle about the line of intense destructive effect. An important source of damage consists of explosions or fires that may be initiated by the jet if it should pass through a magazine or a fuel supply.

The effectiveness of a propelled shaped-charge weapon, unlike that of an armor-piercing projectile, is a property of the charge itself and not of the velocity with which it strikes the target. In fact, for reasons to be considered later, the effectiveness is actually less at higher velocities. The shaped-charge is therefore ideally suited to low-velocity projectiles, such as the Bazooka, and to stationary demolition charges. The armor-piercing projectile, on the other hand, by carrying the main charge through to the other side of the target, will do more general damage there.

Explosive Filling and Charge Length

In general, the depth of penetration by a cavity charge increases with the power of the explosive filling. Cast Composition B is about 20% more effective than cast TNT. One of the most effective explosives is fluid 70/30 Cyclotol. For filling small weapons, this latter composition is too thick (it must flow evenly into the narrow converging space at the base of the liner), and 65/35 Cyclotol is more acceptable.[32] For historical reasons related to the supply of RDX and also to questions of fluidity, many American shaped-charge weapons, including even the howitzer shell, have been loaded regularly with cast 50/50 Pentolite. The depth of penetration with Pentolite is only 90 to 95% of that obtained with 65/35 Cyclotol; at the same time, Pentolite is a more sensitive filling. Picatinny Arsenal has recently developed the ternary mixture PTX-2 (PETN/RDX/TNT 25/44/28) as a castable filling for shaped-charge applications, but it has not yet been adopted for general service use. The Germans have made much use of charges consisting of pressed preformed pellets of waxed RDX and other explosives.

As the charge length, measured from the liner base, is increased, the cavity effect approaches a limit attained at a charge length of about 3 diameters. When the charge length is increased further, there is little increase in depth of penetration. Figure 1, for unconfined 1⅝-in. diameter charges bearing M9A1 steel cones, is illustrative. The charges consisted of 50/50 cast Pentolite topped by pressed tetryl booster pellets ⅝ in. in length. The charge length in Figure 1 includes the booster.

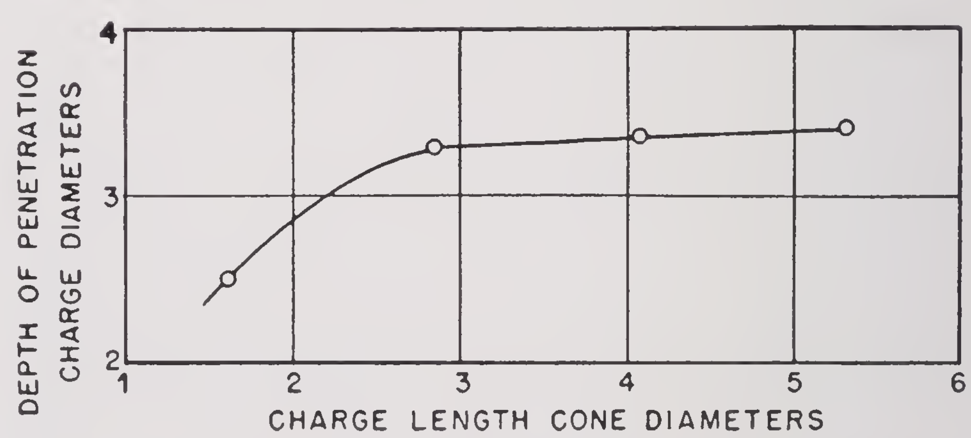

Figure 1. Depth of penetration versus charge length unconfined, 1⅝-in. diameter charges bearing M9A1 steel cones at 3-in. stand-off.

The shaped-charge effect depends upon a concentration of the energy normally leaving the end of the charge. Except for the rather small loss in charge weight due to the presence of the cavity, the general blast and fragmentation effects of a cavity charge are, therefore, practically the same as for an ordinary charge of the same size. Thus, the M6A3 2.36-in. HEAT rocket is an excellent fragmentation grenade. In fact, comparative tests made with an experimental

fragmentation head in place of the shaped-charge head showed that the original shaped-charge head was actually superior for fragmentation. The presence of the cavity, of course, had nothing to do with the superiority, which was due to the rather high charge weight to casing weight ratio as compared with the conventional heavy-walled grenade; but it is evident that one need not sacrifice ordinary high-explosive effectiveness to any appreciable extent in order to obtain the advantage of the cavity effect.

Stand-Off

Most cavity charges show an increase in depth of penetration when the stand-off, or distance between liner base and target, is increased from zero to some optimum distance, which is of the order of several charge diameters. Exceptions are unlined charges and charges bearing 20° steel cones; these perform best at zero stand-off. For all other lined charges, the optimum stand-off increases as the cone apex is increased. Typical depth of penetration versus stand-off curves for steel conical liners of 1⅝-in diameter in unconfined charges are shown in Figure 2. For steel

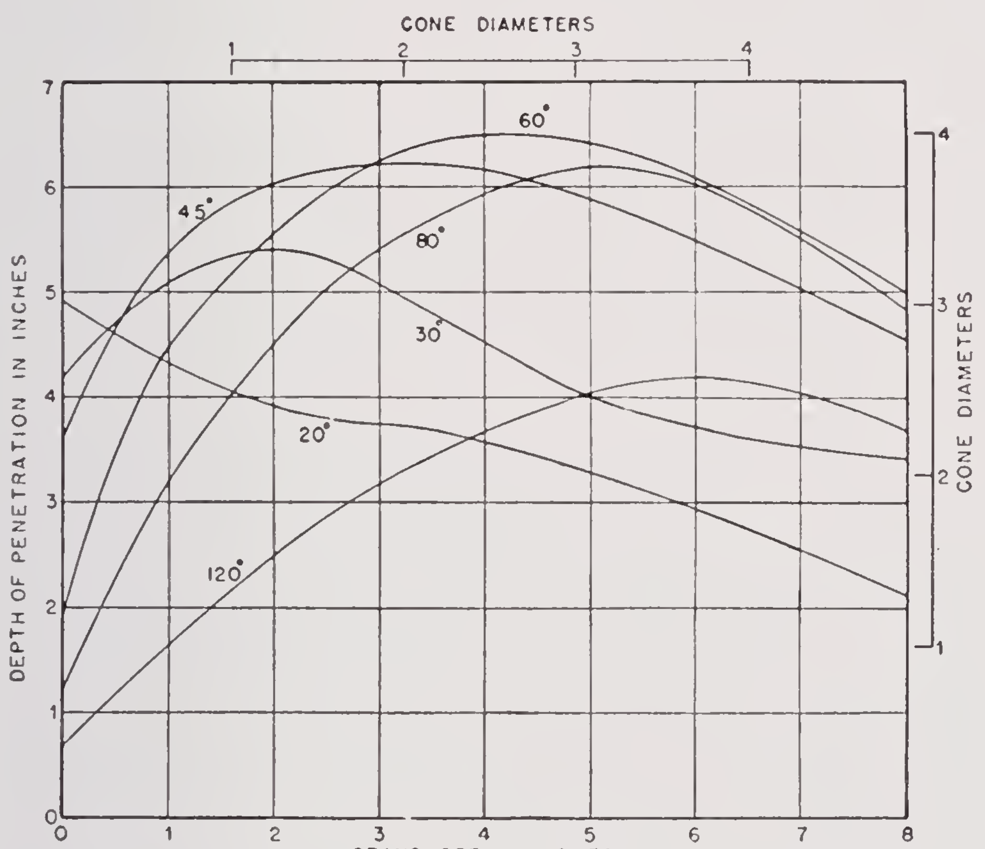

Figure 2. Effect of stand-off on depth of penetration, 1⅝-in. diameter unconfined cone charges.

hemispherical liners, the optimum stand-off is 3.5 to 4.0 charge diameters.[33] At stand-offs in excess of the optimum, depths of penetration are likely to be erratic; occasional charges that are presumably exceptionally well aligned give depths equal to those obtained at the optimum stand-off. Penetration with diminished effectiveness persists out to amazingly large distances from the charge. Thus, one can design charges that will penetrate one charge diameter of mild steel at a stand-off of 15 charge diameters. Aluminum liners show much larger optimum stand-offs than do comparable steel liners.

The hole volume changes but slightly as the stand-off is increased to the optimum for depth of penetration. The improvement in depth is obtained at the cost of some reduction in hole diameter. With increasing stand-off beyond the optimum, the average hole volume shows a decrease. A theory of the effect of stand-off upon target penetration is given in Section 4.3.4.

Liner Thickness

The optimum liner *weight* varies but slightly with the apex angle for conical liners of given base diameter. The optimum liner *thickness* for a given metal is thus proportional to the sine of half the apex angle, though it may be somewhat greater for cones more acute than 45°. While exhaustive tests have not been carried out on metals other than steel, the evidence available indicates that the optimum weight is not very different for different metals, including copper and aluminum as well as steel. At any rate, the performance is not affected critically by the precise liner weight.[34]

The optimum liner weight and thickness are greater for confined than for unconfined charges. In fact, the performance of cones that are of optimum wall thickness in unconfined charges is seriously impaired if the charges are confined. On the other hand, cones that are somewhat heavier than the optimum for unconfined charges show an improved performance when the charges are confined. Optimum wall thicknesses for 45° steel cones under several degrees of confinement are summarized by the following data.

Confinement	Approximate Optimum Wall Thickness for 45° Cones (per cent of base diameter)
None or very light	1.5
Light (cross-sectional charge/casing = 1.3)	2.5
Heavy (cross-sectional charge/casing = 0.4)	3.5

The confinement referred to as light corresponds to that in a rocket head such as the M6A3 2.36-in. HEAT rocket. The condition referred to as heavy corresponds to that in a shell such as the M66 75-mm HEAT shell. The optimum wall thicknesses given are about right also for copper 45° cones.

If one chooses the appropriate optimum cone weight, confinement has no net effect upon the depth of penetration. Increased confinement does increase the hole diameter and hole volume. Other conditions

being constant, increased liner thickness results in smaller diameter holes.

Liner Shape

Liners of various shapes have been tested in small-scale charges. Except for differences in optimum stand-off, a wide variety of shapes appear to be equivalent. No special shape has been discovered that is superior to a cone of uniform wall thickness with apex angle between 45° and 80°. Figure 3 summarizes the depth of penetration versus cone angle relations for steel-lined unconfined 1⅝-in. diameter Pentolite charges. At zero stand-off, 20° cones give the best results of all angles tested, about 3.0 cone diameters in mild steel. Better results, about 3.7 cone diameters in mild steel (equivalent to about 3.1 in armor), are obtained at 2-in. (1.2 cone diameters) stand-off using 45° cones. With unlimited stand-off (e.g., 3 cone diameters), still better results, about 4.0 cone diameters in mild steel (3.2 in armor) are obtained with 60° cones. These maximum depths may be increased by about 10 per cent by using 65/35 Cyclotol in place of Pentolite. Since in most propelled weapons, stand-

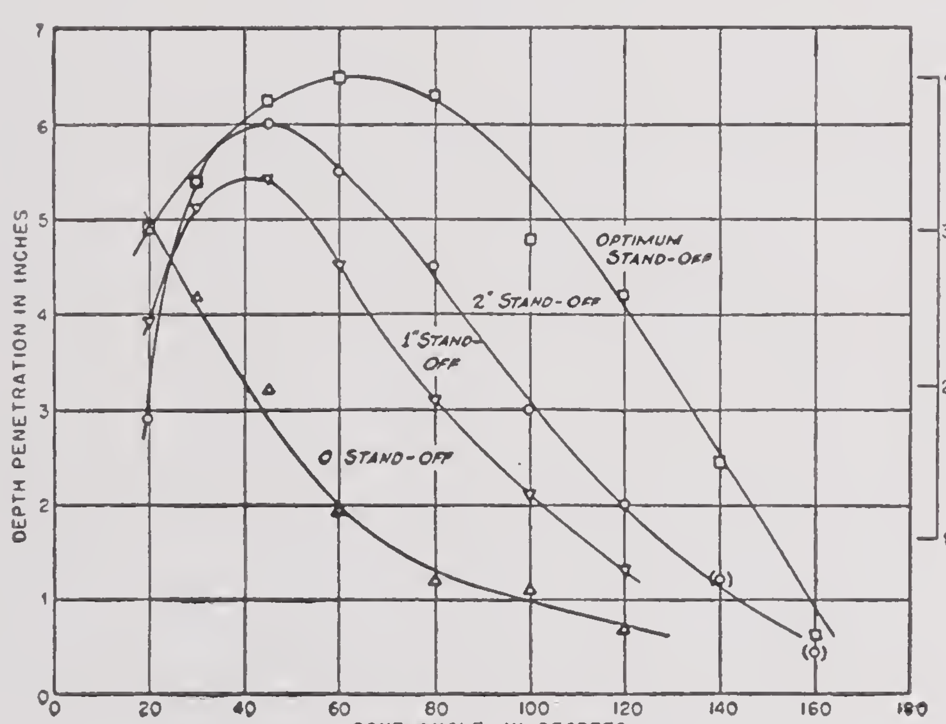

FIGURE 3. Depth of penetration versus cone angle; steel cones, unconfined 1⅝-in. diameter Pentolite charges.

offs much in excess of 1-cone diameter are difficult to obtain, 45° cones appear to be the best choice for such weapons. In stationary demolition charges, however, where stand-off may be readily controlled, 60° cones appear to have a small advantage over 45°.

Cones with tapered wall thickness have received some consideration. For 45° cones, a taper from thin at the apex to thick at the base has an advantage over a taper from thick at the apex to thin at the base, but neither appears to have any advantage over a cone of uniform wall thickness. British sources, however, indicate that a great improvement in the performance of 80° lead cones results from a change from uniform wall thickness to walls tapering from thin at the apex to thick at the base.[35]

Hemispherical steel liners behave much better in confined charges than in unconfined ones. A remarkable improvement has been observed as the result of the presence of an axial flash tube (for point-initiation by a spit-back fuze) but the reason for this phenomenon is not at present known.[36] Hemispherical steel liners are characterized by rather large optimum stand-offs (3.5 to 4.0 diameters) and are quite ineffective at stand-offs of the order of 1 diameter. Steel spherical cap liners with large radii of curvature are ineffective, but British sources indicate that similar liners made of lead perform well.

The configuration of the base of the liner where it joins the casing is of some importance. If the true cone base diameter is smaller than that of the charge and if the cone is supported by a flat base flange covered by explosive, the performance is seriously impaired under certain conditions. In general, for a charge that is confined, the true cone base should be the full diameter of the charge at the place where the cone is secured to the casing. The harmful effect of the base flange when covered by explosive appears to be related to interference with development of the later parts of the shaped-charge jet, normally formed from material coming from near the base of the collapsing liner.[37]

Liner Material

For rather obvious reasons, most shaped-charge projectiles have been equipped with steel liners. The steel should be a mild steel of low carbon content since carburized steel, probably because of its greater brittleness, gives inferior results. Certain service demolition charges, such as the M2 shaped charge, have been provided with glass cones. Glass is somewhat inferior to steel in depth of penetration, but the hole volumes produced in concrete targets are larger and the holes are less filled with debris.[38,39]

Since copper became more available, considerable progress has been made in the development of copper liners, resulting in the adoption in April 1945 of copper cones for the 2.36-in. HEAT rocket (the Bazooka). This development was carried on by the Eastern Laboratory of the du Pont Company under Army Ordnance Department contract. Earlier work[40] with unconfined 1⅝-in. diameter charges had indicated a rather large optimum stand-off for copper,

even though copper was superior to steel at shorter stand-offs.[41] More recent work with copper M6 cones in confined charges (as in the 2.36-in. rocket head) suggests that the optimum stand-off is about the same as for steel, namely about 2 cone diameters for 45° cones. Depth of penetration versus stand-off curves for steel and copper M6 cones are shown in Figure 4.

Up to the optimum stand-off, the depth of penetration by the copper cones is about 40 per cent greater

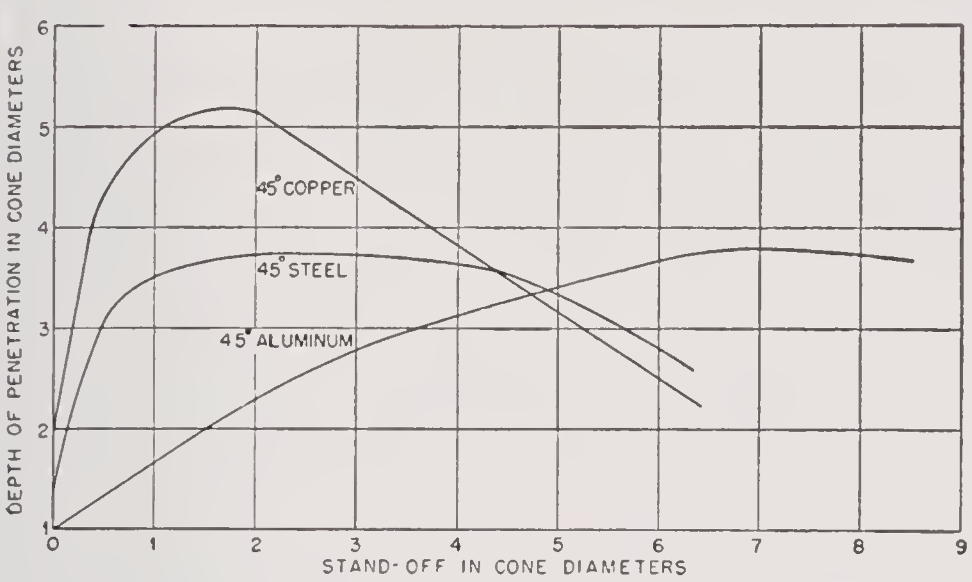

FIGURE 4. Depth of penetration versus stand-off, M6 steel and copper cones (2.36-in. diameter, 0.062-in. wall $1\frac{5}{8}$-in. diameter aluminum 45° cones (0.064-in. wall), all charges steel confined.

than for steel. The maximum depth of penetration is about 5 cone diameters in mild steel or about 3.8 cone diameters in homogeneous armor using Pentolite charges. With 65/35 Cyclotol, these maxima may be increased by about 10 per cent. The relative superiority of copper over steel appears to be somewhat less in an armor than in a mild steel target. At stand-offs beyond the optimum, according to Figure 4, the advantage of copper over steel disappears, though in penetrating through equally large thicknesses of water, copper remains superior to steel. No reason is known why large distances through air should influence the relative performances of copper and steel cones differently from large distances through water. For that matter, no generally accepted explanation has been offered for the quite impressive superiority of copper over steel at moderate stand-offs. One suggested explanation is based on the greater ductility of copper, presumably maintained even under high stress, which may result in more material being pulled from the base of the liner after collapse is complete in the so-called "secondary" phase of jet formation. This material would add to the latter portion of the jet and thereby increase the overall penetrating power.

Aluminum liners are peculiar in that they show remarkably large optimum stand-offs. Figure 4 shows this for 45° aluminum cones. At their optimum stand-off of 6 to 8 cone diameters, penetration by the aluminum cones is about equivalent to the maximum for steel cones. At stand-offs of 1 to 2 cone diameters, however, where steel and copper are most effective, aluminum is quite ineffective. Aluminum cones show a dependence of optimum stand-off on cone angle similar to that observed with steel cones, but for any given angle the optimum for aluminum is displaced to a much larger value than for steel. No plausible explanation of the stand-off effect with aluminum has been offered. The obvious correlation with low liner density breaks down when one considers glass cones which show no such effect.

German sources have indicated that die-cast zinc has merit as a shaped-charge liner material, though it is not in the same class as copper.

The British, early in World War II, drew a distinction between "fluid" and "particle" jets.[42,43] They believed that the more volatile metals such as lead, tin, and cadmium gave rise to fluid jets, whereas steel gave rise to a stream of discrete particles. At one time they regarded the fluid jets as having appreciably greater penetrating power than the particle jets. The comparison however was based upon shallow dish-shaped liners. We know that such liners made of steel are greatly inferior to acute cones, whereas when made of lead they give reasonably good performances. We believe it is correct to state that none of the so-called fluid types of liners is superior to the better steel cones. The distinction between the properties of fluid and particle jets was based to a considerable extent upon the shapes of the holes they produced in the target. We know now that the hole size and shape reflect only in a very indirect way the shape of the jet, depending rather upon the nature of the target and the rate at which momentum is delivered to it. The nature of jet formation by steel cones has been greatly clarified by flash radiographic investigation. The steel jet certainly appears to be formed in a manner reminiscent of the behavior of true liquid jets and the theory of its formation is actually based upon hydrodynamic principles. Whether the jet itself consists of a continuous quasi-liquid stream or a succession of small discrete particles is not definitely known, but the question is probably meaningless. The distinction between the flow of a true liquid and that of a solid under conditions of extremely high stress is rather difficult to define in terms of effects upon the surroundings. For the so-called fluid metals of the British investigators, the relatively low melting and

boiling points make it reasonably certain that the liners actually are melted and, perhaps, to a certain extent even vaporized during jet formation. We should expect that if appreciable conversion to the vapor state takes place the resulting jet will have a tendency to diffuse more rapidly with increasing distance from the target than would the jet from a metal that shows a greater tendency to cohere. Flash radiographic investigation should provide the answer to this point, as well as to the question why lead dish-shaped liners are so much more effective than liners of similar shape made from steel.

A special use was found for composite liners consisting of sand particles bonded by a thermosetting plastic matrix molded to shape. The object was to demolish beyond recognition a small radar oscillator, located within a container. A steel-lined cone charge of conventional design would merely drill a hole through the unit but leave it otherwise recognizable. The sand liner, by producing a more diffuse if less penetrating "jet," was completely effective in disintegrating the target. This application is discussed in Section 3.6.

Target Material

For experimental purposes, many shaped-charge tests have been made using mild steel targets, but homogeneous armor and reinforced concrete are the principal target materials against which most actual weapons are designed to be effective. For quite a wide range of steel cones, the depth of penetration in homogeneous armor averages about 84 per cent of the depth in mild steel. For copper cones, however, the ratio appears to be somewhat smaller, about 74 per cent for copper M6 cones. The hole diameters in armor are about 80 per cent of the diameters in mild steel.

For lack of adequate test facilities, Division 8 did no work with shaped charges against reinforced concrete. A large body of information is available through the work of the du Pont Eastern Laboratory in designing shaped demolition charges for the Engineer Board (contracts W-145-ENG-467 and W-670-ORD-4331).[38,44-47] The depth of penetration in reinforced concrete is roughly 3.2 times the depth in homogeneous armor for the glass-lined M2 shaped demolition charge.

Scaling Laws

Such experimental evidence as is available for large shaped charges indicates that they satisfy a linear or Hopkinson scaling law. If one increases all of the charge dimensions in a fixed proportion, including diameter, liner thickness, charge length and stand-off, the depth of penetration in a given target material also increases in the same proportion. Fairly good evidence of this for a spaced target was obtained in an investigation dealing with the design of shaped-charge bombs.[49]

Aberrations in Cavity Charges

Cavity charges are peculiarly sensitive to any disturbances in symmetry. They are, therefore, more touchy than ordinary charges with respect to design, manufacture, and loading. Thus, if the cone[e] is inclined by as much as 1° or displaced by as much as 1% of the diameter with respect to the charge axis, a significant impairment of the depth of penetration follows.[50] The liner itself must show no variation in wall thickness in a plane normal to the axis, though axially symmetrical variations from apex to base may be tolerated to some extent without causing injury to the performance. Some difficulty has been experienced in obtaining liners for experimental purposes having reproducible qualities. Rather subtle variations in liner quality may result in differences in penetration of as much as 20%. The production of steel and copper liners in quantity showing reasonably uniform behavior has been solved by the operation of successive drawings, nine draws being used to form the 45° M6 and M9A1 cones. Even then, small variations in the behavior of different production lots have been observed.

The explosive charge must be of unusually high quality to ensure satisfactory shaped-charge performance. Penetrations as poor as 50% of normal have been observed in a lot of Service-loaded Bazookas containing the normal Pentolite filling that were found by radiographic inspection to have holes in the castings. A significant difference has been noted in the performance of 70/30 fluid Cyclotol, depending upon the manner in which the charges are cast. This explosive is rather viscous for loading small charges and gives a performance no better than that of Pentolite if loaded in the usual way in cold molds or casings. If the molds are preheated and the centers of the charges kept open by use of risers and steam fingers to eliminate contraction cavities, the performance is improved by as much as 20%.

The effects of these aberrations as well as of certain

[e]Variations in the thickness and quality of the cones can be detected by a radiographic technique.[51]

others, such as wires through the cone and charge (for electromagnetic point initiation), have been discussed in detail.[32] Other interesting experiments on similar lines have been carried out by du Pont Eastern Laboratory.[46,47]

Effect of Spinning

A serious deterrent to the development of shaped-charge shell has been the general deleterious effect of spinning upon the depth of penetration. For some time, this effect was not recognized in this country, though tests conducted by the British had shown its existence.[52] In fact, the HEAT shell for the 57-mm recoilless gun was designed by the Small Arms Division of the Ordnance Department with the expectation that it would supplant the Bazooka. Tests that had been conducted previously at the Explosives Research Laboratory showed that a depth of penetration only half that of a nonspinning round of the same caliber could be expected.[53,54] The problem was for some time obscured by the question of fuze performance and attainment of adequate stand-off at moderately high velocities (of the order of 1,200 fps).

The general effect of spinning at such rates as are necessary to stabilize projectiles at velocities of 1,200 fps is to reduce the depth of penetration by conical liners at optimum nonspinning stand-off by about 50%. At zero stand-off, the effect of spinning on 45° cones is less, but then one loses the advantage normally obtained in a nonspinning charge with increased stand-off. With still higher rates of spin, the penetration apparently levels off and no further reduction below about 50% follows. On the other hand, the effect begins even at rather low rates of spin, so it is not feasible to reduce the twist or muzzle velocity of the gun unless one is willing to go to such extremes as to alter altogether the tactical uses of the weapon. One cannot eliminate the effect by changing the cone angle, since even 20° cones are affected at zero stand-off (in this case, the jet has some distance to travel within the cone before it strikes the target). The effect is no doubt due to centrifugal force acting to reduce the concentration of the normally extremely small-diameter jet. Flash radiographs of spinning cavity charges taken at the Ballistic Research Laboratory show this.[55]

One general recommendation of Division 8 was that serious consideration should be given to high-velocity shaped-charge projectiles stabilized by fins. No action along this line was taken until very late in the war and no such projectiles have been developed in time to be of use to the Services. At the same time, since the tendency has been in the opposite direction, to stabilize even the rocket-propelled projectiles by spin, intensive research was undertaken to discover liners less affected by spin and even to devise liners specially modified to counteract the effect of spin.

Hemispherical liners showed some early promise, and indeed the effect of spin appears to be more gradual with hemispherical than with conical liners, so that with reduced muzzle velocity or reduced twist some improvement over conical liners could be expected. Such liners, made of copper, were actually adopted in the shell, HEAT, M307, 57 mm, but with the present twist and muzzle velocity of the 57-mm recoilless gun, these liners are probably not superior to a well-designed conical liner. These results are confirmed by spinning tests conducted by J. C. Clark and C. E. Hawk at the Ballistic Research Laboratory.[56] The Germans used a hemispherical steel liner in their 105-mm and other hollow-charge howitzer shell. Although, according to recently captured documents, they discovered the deleterious effect of spinning quite early in the war, they apparently made no determined effort to do anything about it.

In the direction of designing a liner specially modified to compensate for spin, partially successful results have been obtained at the Explosives Research Laboratory using a so-called offset liner.[57] The depth of penetration of such a liner is actually improved over the static performance when the shell is spun. As would be expected, the static performance is below that of an unmodified liner and spinning in the wrong direction impairs the performance below that of the static charge. When spun, however, in the proper direction at the optimum speed, which in principle depends upon the degree of offset, penetrations have been obtained that are significantly better than those obtained with conventional conical liners at the same rotational speed, though still inferior to those of nonspinning conical liners. These initial offset liners however were far from perfectly constructed, both in actual detail, which showed some asymmetry in the dies used to form the liners, and in principle, in that the average degree of offset impressed was not ideal for the given liner shape. Considerable improvement can be expected from future research efforts along this line.

Linear Cavity Charges

Linear cavity charges bearing re-entrant, wedge-shaped liners may be used to produce linear cuts in

the target.[58,59] The maximum depth of the cut in mild steel appears to be about 0.8 charge width. For this application, wedges with 45° apex angle appear to be completely ineffective. The approximate optimum conditions for various stand-offs are as follows:

Stand-off (charge widths)	Best Liner Shape and Material	Wall Thickness (charge width)
0–0.3	80° steel	0.02
0.6	80° steel	0.03
1.0	120° steel	0.03
1.2–1.4	80° aluminum	0.06

Beyond charge-target distances of about 2 charge widths there appears to be no liner that has appreciable penetrating power.

General Applications

For antitank applications, the best shaped-charge weapons developed to date have been low-velocity projectiles such as the M9A1 rifle grenade and the M6A3 2.36-in. rocket. These projectiles are rather small and we may anticipate the development of larger shoulder weapons. With the high-velocity T59 2.36-in. rocket motor, for example, one could design a 3½-in. shaped-charge head that would still have about the same velocity as the present Bazooka and would defeat 12-in. armor. On the other hand, the same motor could be used with a head no larger in diameter than that of the present Bazooka to give a higher velocity and larger effective range. We may anticipate the development of fin-stabilized shaped-charge projectiles fired from recoilless guns with velocities in excess of 1,000 fps. We may expect progress from the development of special liners compensated for spin. Even if the effect of spin could be neutralized, however, there is probably little future in high-velocity shaped-charge projectiles (of 2,700 fps or more velocity), since, when high muzzle velocities are available, true armor-piercing projectiles present a better choice.

Shaped demolition charges for attacking concrete fortifications are available. These are particularly useful in preparation for a follow-up attack with Bangalore torpedoes or other demolition charges placed in the holes. Large rocket-propelled shaped charges should be useful weapons for attacking concrete in situations where guns and anticoncrete shell are not available. Some progress has been made in developing such projectiles.

The Ordnance Investigation Laboratory has made effective use of small linear cutting charges in sectioning loaded projectiles and opening mines for examination.[48,60]

4.3.3 General Underwater Penetration by Cavity Charges

The object of underwater tests with shaped charges is to hole a steel target through an intervening layer of water. A direct application is to attack on submarines, where one would like to pierce the inner hull through the layer of liquid between the hulls. Another application is to the attack of capital ships by shaped-charge torpedo warheads, where several liquid-filled and air-filled bulkheads are to be perforated.

For simple experimental tests, it is convenient to define an underwater *range* or distance through water at which a given charge will perforate steel plate of a given thickness in 50 per cent of the trials. The Explosives Research Laboratory undertook an extensive investigation of 1⅝-in. diameter shaped charges, using generally ½-in. mild steel plate but also other thicknesses as the target.[61] The Eastern Laboratory of the du Pont Company under contract with Division 8 undertook a scaling law investigation with steel cones in 3-in. and 6-in. diameter charges, using ¼-in. plate.[62] The general discussion that follows is based mainly upon those two investigations.

Explosive Filling and Charge Length

The effect of charge length upon the underwater range is about the same as upon steel target penetration in air. Maximum range is attained by a length of about 3.0 charge diameters. At 2.4 diameters, the range is within 90 per cent of the maximum. Increase beyond 3.0 diameters does not increase the range, but the greater charge weight will of course result in improved general underwater shock-wave effectiveness.

The pattern of the underwater blast pressure and momentum about a shaped-charge torpedo warhead compared with that about a conventional one has been investigated.[63] To the sides and rear, the shaped-charge warhead gave peak pressures and momenta practically the same as those of the conventional warhead, despite the smaller charge weight. Ahead, these quantities for the shaped-charge warhead fell to minimum values, below those of the conventional warhead, over a zone about 22½° from the axis. On the axis itself, of course, the shaped charge produced the intense, penetrating jet, with pressure and momentum beyond the range of the measuring instru-

ments. Thus, the shaped-charge effect can be incorporated with little loss in general effectiveness, except for a minor loss over the region noted.

With the notable exception of the aluminized explosives, the range for an underwater shaped charge with different explosives runs more or less parallel to the general blast effectiveness. Torpex, which produces greater general underwater damage than an equal weight of Composition B, is not so effective in producing a shaped-charge effect. It appears likely that the energy released in the reaction of the aluminum is too late to influence the motion of the liner leading to jet formation. Therefore Composition B is the better filling where shaped-charge effectiveness is the primary consideration.

Air Space

Corresponding to stand-off in air, underwater shaped charges require some air space beyond the end of the charge for the development of maximum jet action. The cavity itself must, of course, be kept free of water, otherwise the jet action is completely destroyed.

In a general way, optimum air space for maximum range varies with liner shape and liner material much as optimum stand-off does for steel target penetration in air. The optimum underwater air space is, however, somewhat shorter than the optimum stand-off in air; and for steel cones at least the range continues constant, though individual measurements show more erratic behavior, at air spaces well beyond the optimum. The optimum air space is therefore in effect the shortest air space at which the maximum range is obtained consistently.

Typical results are shown in Figure 5 for unconfined 1⅝-in. diameter cast Pentolite charges (protected from the water by cardboard tubes). Additional data for 20° and 30° cones, not included in Figure 5, indicate that for these liners the optimum air space is zero. One notes the remarkable effect of increased air space on the behavior of the aluminum cones. Whereas the optimum air space for 45° steel cones is about 0.5 cone diameter, the optimum for 45° aluminum cones is about 4.5 cone diameters. This behavior of course corresponds to the large optimum air spaces noted for aluminum cones in air.

There is evidence for supposing that the first few inches of water provide stand-off for later parts of the jet as well as constituting target material for the front of the jet. This evidence is based on experiments in which relatively thin layers of water were backed by thick steel targets and the depths of penetration in the steel observed for different thicknesses of water.

Liner Thickness and Shape

The optimum liner thickness for unconfined charges appears to be slightly greater than for steel target penetration in air, about 2 per cent of the diameter for 45° steel cones. The difference may be due to the mild confinement offered by the water itself. For charges confined in steel, the optimum thickness is greater, as observed in the case of steel target penetration in air. For confined charges, cone wall thicknesses not far from those found best for confined charges in air would be satisfactory. At any rate, the liner thickness does not affect the range critically. The optimum cone *weight* is nearly independent of cone angle in the range 45 to 120°; in other words, the optimum *thickness* is proportional to the sine of half the apex angle. For cones more acute than 45° the optimum weight appears to be greater.

Figure 6 shows the range for various cone angles at 0.5 charge diameter and at optimum air space, using steel cones. The charges were unconfined cast Pentolite. The ranges would be improved about 10 per cent by using Composition B. One sees that at

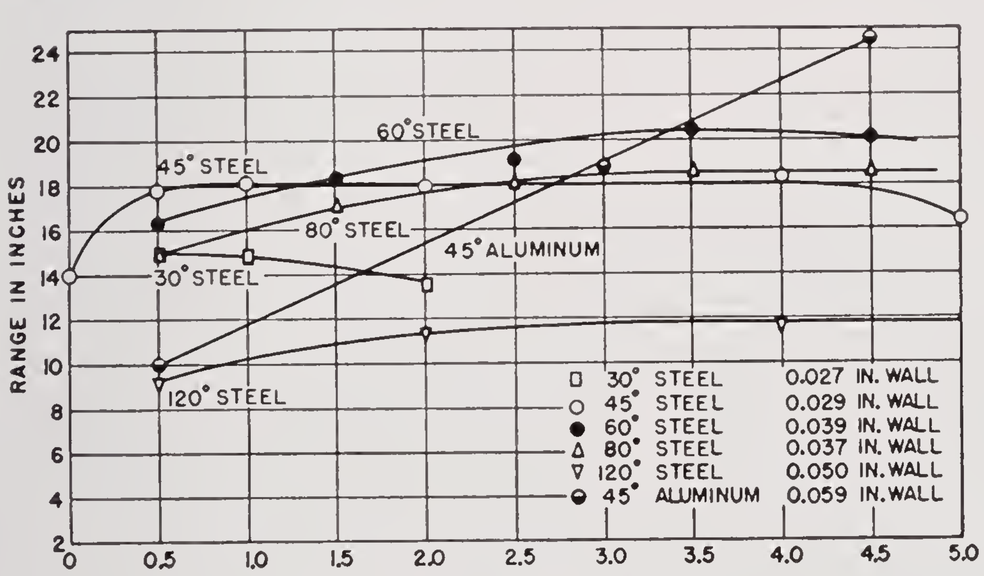

Figure 5. Effect of air space on range, 1⅝-inch diameter cones and charges.

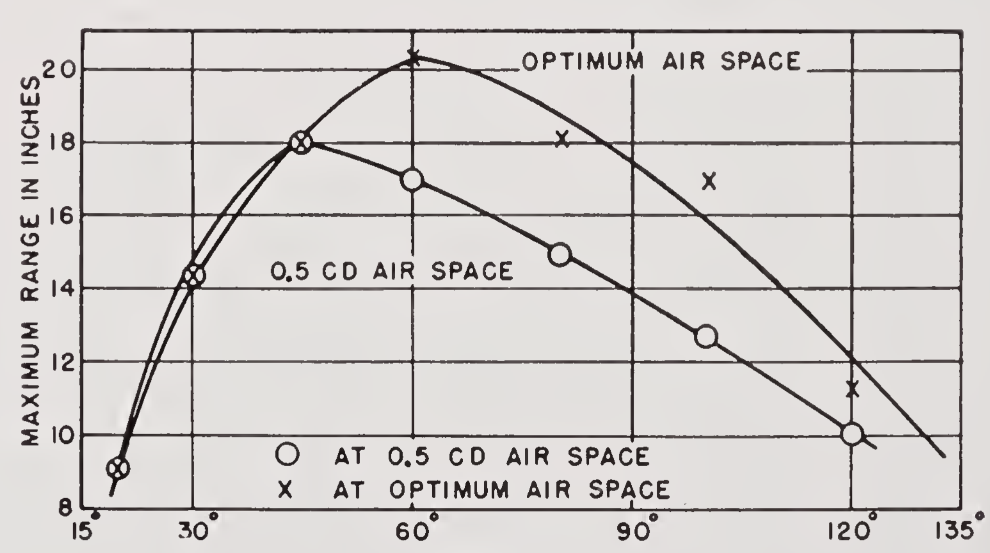

Figure 6. Range versus cone angle, steel cones, 1⅝-inch diameter Pentolite charges.

0.5 charge diameter air space, 45° cones give the greatest range, 11 charge diameters for 0.31 charge diameter mild steel plate. At zero air space, 30° cones would be best, but the maximum range would be inferior to that of 45° cones at 0.5 charge diameter air space. With unlimited air space (3.5 charge diameters), 60° cones give the greatest range, about 12.5 charge diameters. As a matter of fact, an even slightly better range may be obtained using 45° aluminum cones at 4.5 charge diameters air space. Aluminum cones appear to be relatively better under water than in air. Since limitations of space in practical underwater weapons make large air spaces impractical, 0.5 charge diameter using 45° steel or copper cones appears to be the best condition to aim for. Copper shows superiority over steel similar to that observed in steel target penetration in air. The range of a 45° copper cone at 0.5 charge diameter air space is about 30 per cent greater than for a steel cone.

The adverse effect of a flat base flange covered by explosive has been observed in underwater penetration as in air. Confined charges should be designed with the cone base the full diameter of the charge at the place where it is installed.

Underwater Scaling Laws

The underwater shaped-charge effect appears to scale linearly, that is, if one increases the charge dimensions in a fixed proportion, including diameter, length, liner thickness, and air space, and also the thickness of the steel target, the distance through water at which 50 per cent perforations are obtained increases also in the same proportion. A puzzling exception has been noted with small-scale charges against quite thin steel plate. Using 1⅝-in. charges and ⅛-in. mild steel plate, all cone angles between 45 and 100° gave practically identical performances at 0.5 charge diameter air space. This finding was not in agreement with results for 3-in. diameter charges against ¼-in. plate.

One cannot assign a definite water equivalent of steel as target material for the shaped-charge jet. This is not surprising since the latter parts of the jet that have lower velocity than the forward part may penetrate through appreciable thicknesses of water and yet create pressures in steel well below the yield point. If one plots depth in steel versus thickness of water penetrated, for moderate thicknesses of water (great enough to overcome the stand-off effect previously mentioned) 1 in. of water is equivalent to slightly more than 0.5 in. of steel in defeating the jet from a steel cone (less in defeating the jet from an aluminum cone). For large thicknesses of water, however, the depth in the steel tails off more gradually, so that 10 or 12 in. of water in this range may be the equivalent of only 1 in. of steel.

General Applications

The most immediate general applications of the underwater shaped-charge effect are to antisubmarine bombs and to torpedo warheads. These developments are described in Chapter 3.

Linear cutting charges appear to be rather ineffective under water. The depth of the cut, at best 0.8 charge width in mild steel, falls off rapidly with increasing thickness of water between the charge and target. Two charge widths of water will almost completely dissipate the cutting effect of the best linear charge.

4.3.4 Theory of Jet Formation and Target Penetration

Mechanism of Jet Formation

The nature of cone collapse and jet formation has been made clear through exploitation of the flash radiographic technique by J. C. Clark and L. B. Seely at the Ballistic Research Laboratory in this country and independently by J. L. Tuck in Great Britain.[64,65] Flash radiographs of ½ to 1 microsecond duration have shown the various stages leading to formation of the jet and have given some idea of its dimensions. For ¾-in. diameter 45° steel cones, for example, the jet diameter is the order of only 1 mm. Hemispherical liners have been shown to behave differently, turning inside out instead of collapsing like acute cones.[66,67] The spreading of the jet under the influence of high-speed rotation has also been shown.

Confirming evidence has been obtained from explosive flash photography.[68,69] Interpretation of these pictures was at first obscured by the presence of an opaque shock wave surrounding the jet in air or in propane when the latter was used to quench luminosity. When the jet was photographed in a vacuum, however, pictures similar to those obtained by the flash radiographic technique resulted.

In the light of the flash radiographic evidence, a theory of jet formation was developed independently by G. Birkhoff in this country and by J. L. Tuck and G. I. Taylor in Great Britain.[70-72] By drawing an analogy with jet development from converging sheets of liquid (representing the cone surface under pressure far above the yield strength), equations were

deduced, based on hydrodynamic principles, relating the masses going into the high-velocity jet and the slug-like residue to the angle at which the walls meet, directly observed in flash radiographs of early stages of liner collapse.

$$\frac{\text{Mass in jet}}{\text{Mass in slug}} = \frac{\sin^2 \beta}{2}, \qquad (1)$$

where β is the half-angle included between the walls. This β is not the same as the original cone half-angle α but is related to it through the ratio of the velocity with which the liner is projected from the explosive cavity wall to the detonation velocity of the explosive.

$$\frac{\text{Velocity of projection}}{\text{Velocity of detonation}} = \frac{\sin(\beta - \alpha)}{\cos \alpha}. \qquad (2)$$

Equations were derived also for the relative jet and slug velocities.

If one attempts to deduce the mass in the jet merely by subtracting the total slug mass from the total mass of the original cone, one will be in error; since at a late stage in cone collapse, at least with unconfined charges having the same diameter as the cone base, the slug pinches off from the skirt of the cone, leaving an appreciable amount of the latter to fragment into relatively coarse, slow-moving pieces that probably have little penetrating power. Interesting experiments to show this process were conducted at the Explosives Research Laboratory using explosive charges of reduced power.[73] Several techniques were devised for measuring the true contributions of mass to the jet from various parts of the cone, of which the simplest is to fire presectioned cones into a tank of water, recovering and weighing the slug segments.[74,75] These measurements turned out to be consistent with equation (1), at least for the apex halves of the cones, in that values of β were deduced that agreed reasonably well with the values observed by flash radiography, taking into account the difference in the scale of the charges. For a 1⅝-in. diameter 45° steel cone of 0.037-in. wall thickness in an unconfined charge, about 50 per cent of the cone's mass goes into the slug and about 20 per cent into the high-velocity jet.

The lower halves of the cones, according to the slug recovery technique, show a rapidly increasing ratio of mass in the jet to mass in the slug as one approaches the region at which the slug pinches off. It is difficult to reconcile this increase with the ideal hydrodynamic process represented by equations (1) and (2). The flash radiographs show, however, that material continues to be pulled from the base of the slug for some time after collapse is complete. Birkhoff has termed this the secondary phase of jet formation but has attributed it to squirting from within the slug because of the hydrostatic pressure acting on it. Birkhoff's mechanism for this effect seems improbable because the pressure is certainly not any greater than that driving the liner together in the first place. It appears possible instead that the slug, under enormous hydrostatic pressure, is pulled out by tension resulting from continuation of the same inertial forces that lead to separation of the jet from the slug originally. The appearance of the slug during late stages of jet formation is strongly reminiscent of Bridgman's metal specimens that have been strained by tension while under a hydrostatic pressure of 25,000 kilograms per square centimeter.[76,77] This speculation is interesting because the greater ductility of copper would then give rise to a greater quantity of material drawn into the latter part of the jet during this secondary phase of jet formation, thereby accounting plausibly for the superiority of copper over steel as a cavity charge liner material.

A weakness of the Tuck-Taylor-Birkhoff ideal hydrodynamic mechanism is that it fails to account directly for the well-established velocity gradient that exists in the jet. It can be made to do so by an assumption concerning the distribution of velocity with which the liner is projected,[78] but one would then like to have a theoretical treatment of this process. It is possible, on the other hand, that the so-called secondary phase of jet formation contributes more heavily to the overall performance than has been generally recognized. At any rate, the primary hydrodynamic mechanism is essentially correct for development of the leading part of the jet, coming from the apex half of the cone. It represents the major theoretical advance to date in the treatment of cavity charge phenomena.

Theory of Target Penetration by Shaped-Charge Jets

A theory of target penetration was presented in an early report from the Explosives Research Laboratory.[79] The theory of jet formation also advanced in that report was shown subsequently by the flash radiographic evidence to be wrong, but the theory of target penetration, based to a considerable extent upon optical observations of jet velocities and penetration velocities appears to be essentially correct.

One assumes that since the pressures developed in

the target by jet action are in general far above the yield strengths of common target materials, including steel, the resistance to penetration may be calculated approximately in the same way as one calculates the resistance encountered by a fragment in passing through a fluid. The resulting equation for the velocity of penetration takes the form:

Case I $$\frac{U^2}{V(V-U)} = \frac{2}{d}\frac{m}{A},$$

Case II $$\frac{U^2}{V(V-U)} = \frac{1}{d}\frac{m}{A},$$

Case III $$\frac{U^2}{(V-U)^2} = \frac{1}{d}\frac{m}{A},$$

where U is the penetration velocity, V the jet velocity, m the mass per unit length of the jet, A the jet cross-sectional area, and d the target density, depending on the motion of the jet particles after striking the target. Case I corresponds to elastic impact, the jet particles recoiling with the same momentum they had originally but reversed in direction (a more refined treatment would take account of the forward motion of the impact surface). Case II corresponds to the situation in which forward momentum of the jet particles is annihilated, the particles moving to the side. Case III corresponds to the situation in which the jet particles are slowed down to the same forward velocity that is acquired by the target material. It is not possible in the present state of our knowledge to tell which situation or which cross between situations actually exists during target penetration by shaped-charge jets. For immediate practical considerations, however, the differences are of less importance than the general form, which suggests that the penetration velocity should depend only on the target density and not on its strength. This was confirmed by optical determinations of penetration velocities through various materials ranging from water through lead. The depth of penetration also, to a first approximation, should depend for a given charge only on the inertia of the target, but the hole diameter on the other hand should depend on interaction between the rate of penetration and the strength of the target. It was pointed out, however, that when the process of so-called primary penetration was over and the jet all consumed, the material in the target would have some forward momentum. Plastic flow would therefore continue until the forces were reduced to about the elastic limit. This process, referred to as secondary penetration, would have the effect of deepening the hole somewhat, to an extent depending on the target's strength. These ideas were confirmed by direct experimental evidence. Thus, while the depth of penetration by the $1\frac{5}{8}$-in. diameter M9A1 cone charge (45°, 0.037-in. wall steel cone) in an all-lead target is about 8 in. compared with 5.40 in. in an all-steel target, the overall depth in a target consisting of 2 in. or 4 in. of lead backed by steel to reduce secondary penetration to the same level encountered in the all-steel target is actually less (5.37 in. and 4.81 in. respectively for 2 in. and 4 in. of lead) than in the all-steel target, showing the greater resistance to primary penetration by the denser lead medium.[80] Similar experiments going in the opposite direction were made with aluminum targets. At the same time, the hole diameter in lead is many times larger than the diameter in steel. The shape of the hole thus has no direct connection with the shape of the jet. One may actually fire the jet through a small hole (larger, of course, than the true jet diameter) in a steel plate without enlarging the hole, though the hole that would be produced by the jet in passing through a similar unholed plate may be considerably larger.[81]

The jet was assumed to consist of a train of independently moving particles covering a certain effective cross-sectional area A about the axis but with a negative velocity gradient from the tip to the rear. This was shown by velocity measurements determined optically after the jet had passed through various thicknesses of steel. The leading velocity of the jet emerging from a given thickness of target decreases with increasing target thickness and is furthermore consistent with the supposition that the particular part of the jet involved had been traveling uniformly with that velocity all the way from the charge. Later parts of the jet therefore do no work on the forward part of the target, which is opened up independently by preceding parts of the jet. The effect of stand-off was explained as due to the lengthening of the jet (decrease in the term m of case III) resulting from the velocity gradient with increasing distance from the charge. At extremely short stand-offs, the jet is in a sense inefficient in penetrating the target; momentum is delivered at a rate too fast for the target to be pushed out of the way. Under this condition, more of the jet is consumed in the forward part of the target than is necessary and this inefficiency is reflected in the greater entry diameter of the hole produced and also in a slower rate of penetration. As the stand-off is increased, the jet becomes more efficient

in that the decrease in penetration per unit length of jet is more than compensated for by the increased length of the jet. If this were the only consideration, one might expect the depth of penetration to go on increasing with increased stand-off (the hole diameters at the same time decreasing) until the jet density became so attenuated by lengthening that the rate at which momentum was delivered per unit cross-sectional area (the stagnation pressure) approached the yield strength of the target. Since, however, different segments of actual jets are never perfectly coaxial, the jet has a tendency to spread (one sees indications of this in flash radiographs) or increase in effective cross-sectional area with increasing distance from the charge. This spreading makes the jet less effective, and, eventually, the spreading becomes more important than lengthening, so the depth of penetration passes through a maximum at a stand-off of the order of several charge diameters. At larger stand-offs, the average depth of penetration decreases but at the same time becomes more erratic, so that an occasional charge, presumably more perfectly aligned than ordinarily, will show an exceptionally good penetration, comparing favorably with the average obtained at the shorter so-called optimum stand-off.

By assuming a "reasonable" value for the ratio m/A (e.g., 1 to 2 g per cubic centimeter for the M9A1 jet at moderate stand-off), one may arrive, by selecting one of cases I to III, at calculated values for the rates of penetration through various target materials in quite good agreement with the observed values. For a more quantitative treatment, however, detailed information concerning the jet structure is needed, in particular the cross-sectional area and linear mass distribution of the jet. Some effort to determine the latter quantity was made through jet momentum and kinetic energy measurements,[82] but the interpretation of these quantities is uncertain due to the fact that unknown quantities of momentum and energy are lost through material blown out of the hole. The total momentum and kinetic energy of the 1⅝-in. diameter M9A1 cone charge appear to be about 3.8×10^6 g per centimeter per second and 10,400 calories respectively, but the way in which these quantities are distributed among the various parts of the jet is not easily determined. The jet diameter could, in principle, be determined by flash radiography but the resolution is at present not fine enough for the measurements to be other than rough estimates of the order of magnitude. In the absence of experimental methods for determining accurately these two essential properties of the jet, efforts to develop a quantitative theory of target penetration were abandoned though the present qualitative theory appears to account in a simple way for the various penetration phenomena that have been observed.

Jet Velocities and Penetration Velocities

Shaped-charge jet velocities and penetration velocities through various target materials have been measured with the rotating drum camera. The leading velocity for the jet (actually the velocity of the luminous shock wave created in air by the jet) from a 1⅝-in. diameter 45° steel cone is of the order of 7,500 mps using a Pentolite or a Composition B charge. The velocity decreases with increasing liner mass and appears to be independent of the particular metal constituting the liner. For given liner mass, it decreases also with increasing cone apex angle. The velocity is atonishingly persistent in air, remaining practically constant out to at least 10 charge diameters from the charge.

As mentioned previously, the jet velocity shows a negative gradient from the tip to the rear, shown by determining the leading velocity after penetrating through various thicknesses of target. The following approximate values are representative for 1⅝-in. diameter M9A1 cone charges at 6-in. stand-off.

Thickness of Steel Penetrated (in.)	Leading Velocity Emerging from the Target (m/sec)
0	7,700
1	6,400
2	4,800
3	3,300

This cone will penetrate normally through about 5 in. of mild steel. The slowest part of the jet consists of the slug, which for the M9A1 cone (25 g without flange) weighs about 13 g and probably has a velocity of about 400 mps. The slug velocity cannot be measured by optical methods but it may be inferred from flash radiography. The slug evidently contributes nothing to the penetrating power of the jet, but it is considered to be a formidable secondary projectile in its own right if it can get through the hole in the target.

The penetration velocity for a given jet, as mentioned previously, is a function of the target density. For the 1⅝-in. diameter M9A1 cone at stand-offs not less than the optimum for depth of penetration, the average rate of penetration through the first inch or two of mild steel is about 2,500 mps.

Shaped Detonation Waves

There has naturally been much speculation whether the cavity effect can be improved by tailoring the shape of the detonation wave to fit the liner more perfectly. The first concrete suggestion for accomplishing such an adjustment in wave shape appears to have been made by H. J. Poole in Great Britain.[83] He proposed using a core of low-velocity explosive surrounded by a shell of high-velocity explosive, adjusting the shape of the boundary between them to obtain any desired wave shape. By using a simple cylindrical core and shell, a cone-shaped wave may be produced in the core. With a cast TNT core and a cast Pentolite shell, improvement of the order of 15 per cent over straight Pentolite was actually obtained with a number of types of small-scale cavity charges both in steel target penetration in air and in underwater range.[84] The effect proved to be rather temperamental when applied in certain actual weapons,[40] though in no case was the performance inferior to that of an all-Pentolite charge. Improvement was observed also using an inert wooden core in a Pentolite surround, terminating the core a short distance above the cone apex so that the cone would be completely covered by explosive. In this case, the wave shape was modified presumably by peripheral initiation of the explosive near the cone. A further improvement in performance, additive to that produced by the core, was observed on relieving the confinement towards the base of the charge. The reason for this effect is not known, but charges were prepared having both TNT cores and relieved confinement that gave depths of penetration as much as 30 per cent above normal.

Further experiments have been made using Baratol cores and Composition B surrounds.[85] The greater difference in detonation rates permits one to modify the wave shape more drastically. Improvement over straight Composition B was actually observed, but the advantage was rather small. The low power of Baratol no doubt neutralizes most of the advantage obtained from shaping the detonation wave. We need for this purpose a high-powered explosive having a low detonation rate. Many interesting phenomena were observed in the Baratol-cored charges through which an acute cone-shaped detonation wave was propagated. Under certain conditions, an intense Mach wave appeared in the center of the core that resulted in amazingly deep central pits when the flat-ended charges were fired resting on steel plates in the standard plate-denting brisance test. Related studies of Mach effects in air are described in an early report.[86]

4.3.5 Fuzing of Shaped-Charge Weapons

The fuzing of shaped-charge projectiles at moderate to high striking velocities raises a problem because of the requirement of preserving stand-off. At low striking velocity, such as the 270 fps attained by the M6A3 2.36-in. HEAT rocket, fuzing may be successfully accomplished by means of a sensitive base-detonating fuze, though even here one must be careful. At higher velocities, the problem is more difficult to solve with a base fuze. The early T20 models of the 57-mm HEAT shell at 1,200 fps were giving no penetration at all, the shell crushing all the way back until the main charge was initiated by impact before the T94 base-detonating fuze functioned. The M67 105-mm HEAT shell equipped with the standard M62 BD fuze has been shown by high-speed photography at the Ballistic Research Laboratory to be firing at little better than zero stand-off, the ogive crushing almost through its entire length before deceleration is sufficient to activate the fuze. In this case, the loss in stand-off does no particular injury to the performance, which is impaired more seriously by the spin of the shell.

One may reduce fuze delay to a minimum by using a point-initiating fuze. Such a fuze has the advantage that the functioning time is a property of the fuze and not of deceleration of the entire projectile. For shaped-charge applications, one requires a fast method of transferring the initiating impulse from the nose to the base, since it is essential for the development of the cavity effect that the main charge be initiated from the end opposite the cavity. At the same time one must avoid as much as possible introducing material on the axis of the charge in the path of the main jet. Within the cavity, any obstacle whatever close to the axis will destroy the cavity effect almost completely. Even ahead of the cavity, however, an obstacle such as a long firing pin, common in many types of point-initiating fuzes, will serve as so much added thickness of target material. The fact that the pin is slender makes little difference because as seen from flash radiographic evidence, the jet is even finer, and to the jet, the pin therefore presents an obstacle as formidable as a plate of metal as deep as the pin is long.

Shaped-Charge Spit-Back Fuze

With these considerations in mind, Division 8 applied considerable energy to developing the principles of point-initiation of shaped-charge projectiles by means of a miniature shaped-charge element in the

nose which would fire back down an axial flash-tube to a tetryl booster at the base of the projectile.[36] This research led to the development by Picatinny Arsenal of the service fuze, PI, M90, standard in the M307 57 mm HEAT shell. This fuze bears a one-piece so called auxiliary detonator cup made of aluminum having a re-entrant 0.014-in. wall 80° cone in the base. The diameter is ⅜ in. and the unit is loaded with 2.1 g of pressed 50/50 Pentolite. To eliminate the need for a firing pin, the fuze is initiated by means of a percussion-sensitive detonator in the nose, flashing down a short hollow tube to the main detonator housed in the arming rotor. This method of initiation, however, is not sensitive to ground impact. The British No. 233 fuze is based on similar principles.

The miniature shaped-charge element develops a jet with a velocity of the order of 7,000 m per second. There is negligible delay (of the order of 1 microsecond) in the initiation of tetryl eight inches or more away when struck by the jet. The estimated overall functioning time of this type of fuze in a small projectile, the size of the 57-mm shell, is about 50 microseconds. The presence of the axial flash tube running back through the main charge does not impair the depth of penetration in any way. In fact, with hemispherical steel liners, the depth of penetration is remarkably improved by the presence of the tube, for reasons that are by no means clear. There is, however, a reduction in hole diameter over the first caliber or so of penetration in steel plate that is associated with the presence of the tube. For this reason, the spit-back principle cannot be readily applied where a large-hole entry diameter is essential, such as in small follow-through projectiles.

A fairly successful shaped-charge rocket fuze, T-2000, for nonspinning rounds, was developed, though never adopted for Service use, by minor modifications of the Service plastic-bodied M52B1 trench mortar fuze. The conventional booster cup was replaced by the miniature shaped-charge unit and the firing pin was replaced by a plastic adapter holding one of the percussion detonators used in the M90 fuze. The M52B1 body was not ideal for the purpose, but it did contain approved setback arming elements. The original 1¼-in. metal firing pin, if retained to ensure functioning on ground impact, seriously impaired the depth of penetration, as expected. Some experimental work was done in collaboration with Allegany Ballistics Laboratory on a plastic firing pin for this fuze, which seemed to be suitable if it could be made to function on ground impact as well as against plate, for the 2.36-in. high-velocity rocket grenade, T59. The results were not particularly encouraging because of mechanical weaknesses of the pins, but a successful fuze could no doubt be developed by following up this line of investigation. The low-density plastic offers considerably less resistance to the jet than does a metal pin.

The shaped-charge spit-back method of initiation has also been applied to the fuzing of experimental 1,000-lb shaped-charge bombs fired statically. The unit was 1 in. in diameter and fired down a 2-in. ID flash tube to initiate the booster about 48 in. away. The Service AN-M103 bomb nose fuze was adapted for the purpose simply by substituting the spit-back element in place of the conventional booster cup, but a less massive body and firing pin would be better suited to the purpose.

Electromagnetic Impact Fuze

An electric impulse may be generated on impact by driving a magnet in the nose through a surrounding coil. This impulse is easily led by wires to an electric detonator at the base of the projectile. The German fuze, Z66, is based on this principle, though not applied to shaped-charge rounds. Division 8 at the request of NDRC Division 3 participated in designing and testing a shaped-charge head for the high-velocity T59 2.36-in. rocket fuzed with an electromagnetic impact fuze, T2003, to be developed by the Bell Telephone Laboratories under contract with Division 3.

The original work on this method of initiation for shaped-charge projectiles was carried on by the Frankford Arsenal (Fuze T16E1). The Bell Telephone Laboratories added engineering refinements to make the unit suitable for production and assembly in large quantities.

The magnet in the nose is a hollow cylinder, providing a hole 0.70 in. in diameter for the jet to shoot through. This leaves the entire axial region ahead of the main charge clear of obstructions. The wires are led back through crimps in the edge of the cone base. To ensure functioning on ground impact, a secondary relatively slow inertia-activated detonator mechanism is located in the base, on the theory that against plate the electrically activated detonator will function first.

Preliminary tests of the complete round, which has a velocity of about 385 fps, gave inferior results that were traced to the presence of excess sealing compound on the cone around the regions where the wires passed through. Subsequent tests with the sealing compound removed gave excellent results. The depths of penetration at normal incidence exceeded 8-in. in

homogeneous armor using 2.118-in. diameter 45° copper cones. This performance was equivalent to that produced by static charges fired at 3-in. stand-off in the entire absence of the fuze mechanisms in the noses. The projectiles performed satisfactorily also at 30° and even at 45° incidence. The indicated fuze functioning time was about 60 microseconds, representing an ogive collapse of less than ½ in. before detonation.

This development was unfortunately started too late to be of any use during the war. The principle is however of considerable value, since it may be readily adapted to weapons of other sizes, including also certain nonshaped-charge projectiles where there is an advantage in a fast point-initiating base-detonating fuze system.[f]

[f]The complete project is described in a joint Division 3, Division 8, and Bell Telephone Laboratories Report.[87]

Chapter 5

THE THEORY OF THE DETONATION PROCESS[a]

THE WORK DONE by various Division 8 contractors greatly strengthened the evidence for the validity of the thermodynamic-hydrodynamic theory of the propagation of one-dimensional detonation waves through solid as well as gaseous explosives. This theory, which originated with Rankine, Hugoniot, Chapman, and Jouguet, is based on the assumption that at the point where detonation takes place there is conservation of matter and energy and that the equation of motion of mechanics applies there. These three almost self-evident assumptions must be supplemented by one additional condition about which there has been a great deal of dispute and discussion, that the detonation velocity will be the minimum permitted by the above conditions. In order to apply these simple principles to any actual case, it is necessary to have information about the equation of state of the products of the explosion as well as a knowledge of the energy as a function of pressure and volume.

The work under Division 8 involved an extension of previous efforts to apply these equations because more elaborate equations of state were employed and the question of the effect of shifting chemical equilibria was explored. The overall results were sufficiently successful, i.e., they agreed sufficiently well with experimental measurements of the detonation velocities of a wide variety of solid explosives over a range of loading densities, so that considerable confidence in the soundness of the basic theory now exists. The significance of this result from a practical viewpoint is that it permits the calculation of the detonation velocities of hitherto unmeasured explosives if the chemical composition and the heat of combustion of the material is known. Furthermore, it shows quite conclusively that the detonation velocity is not a mysterious quantity to be endowed with undue significance, since the theory clearly relates it to the thermochemical properties of the detonation products.

A by-product of these investigations is an estimate of the pressure, temperature, and density of the products of detonation immediately behind the detonation front within a solid explosive. These estimates have proved very useful in later work in which the properties of shock waves in air and water from high explosives were calculated.

The equation of state which seemed to work the best, although designed for a higher pressure region, was not in conflict with that successfully used by others for the lower pressure region involved in propellent powders.

The work summarized in the preceding paragraphs began with the preparation of a review of the literature of the past sixty years on hydrodynamic and thermodynamic theory as applied to detonation and shock waves.[b] Since this review was never issued as a report but was instead circulated in mimeographed form to the group directly interested, its contents are described in some detail in the paragraphs immediately following.

The review begins with a qualitative discussion of the building up of a discontinuous shock front. Then the Riemann formulation of the equations of hydrodynamics is introduced.[1] These equations constitute a statement of the equations of motion and continuity, and, for the plane case with adiabatic flow, they may be written

$$
\begin{gathered}
\frac{\partial r}{\partial t} + \left(u + c\right)\frac{\partial r}{\partial x} = 0\,, \\
\frac{\partial s}{\partial t} + \left(u - c\right)\frac{\partial s}{\partial x} = 0\,, \\
r = \frac{\omega + u}{2}\,, \quad s = \frac{\omega - u}{2}\,, \\
c^2 = \left(\frac{\partial p}{\partial \rho}\right)_s\,,
\end{gathered}
\tag{1}
$$

where t is the time, x the (Euler) coordinate of distance, u the particle velocity, ρ the density, and p the pressure; c is the velocity of small amplitude sound waves. The Riemann function ω, defined by

$$
\omega(p) = \int_{\rho(p_0)}^{\rho} \frac{c}{\rho}\, d\rho\,, \tag{2}
$$

may be increased by an arbitrary constant. Since the

[a]This section is based on a summary prepared by S. R. Brinkley, Jr.

[b]This literature survey by G. B. Kistiakowsky and E. B. Wilson, Jr., is referred to in subsequent reports as *Hydrodynamic Theory of Detonation. Part I. A Literature Survey.* The succeeding parts of the report on *Hydrodynamic Theory of Detonation* have been issued.

[redacted]

pressure and density are connected by the adiabatic law, the Riemann function may be considered a function of either the pressure or the density. From the equations (1) it is evident that r is constant along lines, called characteristics, in the x-t plane such that

$$\frac{dx}{dt} = u + c \quad (r \text{ lines}), \tag{3}$$

and that s is constant along lines in the s-t plane such that

$$\frac{dx}{dt} = u - c \quad (s \text{ lines}). \tag{4}$$

The lines have the following useful properties.

1. There is a line of each type through each point in the x-t plane.
2. If the values of s and r on the lines passing through a given point are known (as, for example, the generating surface) then u and ω are known there. Then p and ρ can be found from equation (2).
3. If lines of a given kind having different values of r (or s) meet in a point, there is a discontinuity in u,ρ at that point.
4. If in a given region s has the same value along adjacent s lines, the r lines are straight in that region.
5. Similarly, if r has the same value along adjacent r lines in a given region, the s lines are straight in that region.
6. For a perfect gas, at least, the curvature of an r or an s line is positive if u increases along the line.

In the report under review, the properties enumerated are employed in a discussion of the building up of the discontinuous shock or detonation front.

A shock wave is produced by the acceleration of some generating surface. A detonation wave is self-maintained through the energy received from the chemical reaction of the explosive.

The equations for the conservation of mass, momentum, and total energy have been employed by Rankine[2] and Hugoniot[3] in the formulation of three conditions relating the pressure p_2, specific volume v_2, and particle velocity u_2 of the medium behind the moving discontinuity to the velocity D of the discontinuity and the pressure p_1, specific volume v_1, and particle velocity u_1 of the undisturbed medium in advance of the discontinuity.

$$\begin{aligned} D &= u_1 + v_1\sqrt{\frac{p_2 - p_1}{v_1 - v_2}}, \\ u_2 &= u_1 + \sqrt{(p_2 - p_1)\,(v_1 - v_2)}, \\ E_2 - E_1 &= \tfrac{1}{2}(p_2 + p_1)(v_1 - v_2), \end{aligned} \tag{5}$$

where $E_2 - E_1$ is the difference in specific energy content of the material behind the front and the undisturbed medium in advance of it. This quantity can be calculated by the thermodynamic relation

$$E_2 - E_1 = \frac{Q}{M} + \frac{1}{M}\int_{T_1}^{T_2} C_v^* dt + \int_{\infty}^{v_2} \left(\frac{\partial E}{\partial v}\right)_{T_2} dv, \tag{6}$$

where Q is the heat (absorbed) of reaction at constant volume per M grams of reactant at the initial temperature T_1, and $C_v{}^*$ is the constant volume heat capacity of M grams of products, gaseous products being considered in the ideal gas state; T_2, the temperature of the detonation front, is related to p_2 and v_2 by an equation of state

$$p = f(T,v). \tag{7}$$

In the case of shock waves, where there is no chemical reaction, equation (6) may be employed with $Q = 0$. The first of equations (5), together with equations (6) and (7), defines a curve in the p_2,v_2-plane for specified values of p_1 and v_1. With an additional relation between p_2 and v_2, these quantities may be determined, and the detonation velocity and particle velocity behind the detonation front are determined by the first two of equations (5).

Chapman[4] and Jouguet[5] postulated that the detonation velocity is the minimum velocity compatible with the other conditions, it then being given by

$$\begin{aligned} D &= u_2 + c_2, \\ D &= u_2 + v_2\sqrt{-\left(\frac{\partial p_2}{\partial v_2}\right)_s}, \\ D &= v_1\sqrt{-\left(\frac{\partial p_2}{\partial v_2}\right)_s}. \end{aligned} \tag{8}$$

Arguments in support of this hypothesis are given in the reports under review and by Becker[6] and Scorah.[7] However, no existing demonstration of the validity of this hypothesis is without theoretical objections, and equation (8) is employed with ad hoc justification of its success in interpreting explosion phenomena, particularly in the case of gaseous explosions where there is no uncertainty as to the form of the equation of state.

If a suitable form for the equation of state (7) exists and if the composition of the products of the explosion reaction is known or can be determined, simultaneous solution of equations (5) to (8) permits the determination of the detonation velocity and of the pressure, specific volume, and temperature of the detonation front. Lewis and Friauf[8] have compared experimental values of the detonation velocities

for the explosion of oxygen-hydrogen mixtures, both with and without the addition of a third, inert gas, with the predictions of theory, employing the ideal gas equation of state. When account was taken of dissociative equilibria of the product gases, good agreement between theory and experiment was obtained.

A study of the calculation of detonation velocities for solid explosives has been made by Schmidt.[9] These calculations are subject to three criticisms. The Abel equation of state,

$$p(vM - b) = nRT, \tag{9}$$

was employed, in which the covolume b is assumed to be a constant and R is the gas constant for M grams of gas. Using observed detonation velocities for the evaluation of b, it was found experimentally that b depended significantly on the density of the gases, a fact which was not taken into account in the derivation of the theoretical equations for the acoustical and detonation velocities. The analysis of the explosion products in bombs at low density was used for the calculation of the composition of the detonation products, a procedure of questionable validity, because it is very likely that the several gaseous equilibria involved are frozen because of too slow reaction rates at uncertain and variable stages of the expansion. Finally a less general energy equation than (6) was employed.

The survey of the literature which has just been reviewed was followed by a report on the calculation of the velocity of detonation of solid explosives.[10] For this purpose a modification of the semiempirical equation of state of Becker was used. This equation of state has been shown to reproduce satisfactorily Bridgman's data for the behavior of nitrogen at room temperature and at densities as high as 1.2 g per cc. Omitting low temperature terms and adopting a $T^{-\frac{1}{3}}$ dependence of the covolume on temperature, the equation of state was written

$$\begin{aligned} PvM &= nRT(1 + xe^{x}), \\ x &= \frac{k}{T^{\frac{1}{3}}Mv}, \end{aligned} \tag{10}$$

where $k/T^{\frac{1}{3}}$ is equivalent to the van der Waals covolume in the limit of low densities. The composition of the explosion products was approximated by the rule that in listing the products oxygen is considered to react first with carbon to form carbon monoxide, additional oxygen reacts with hydrogen to form water, and the remaining oxygen, if any, reacts with carbon monoxide with the formation of carbon dioxide. It was shown that the calculated detonation velocity of the usual organic explosives is insensitive to the composition of products, and the results of rough equilibrium calculations justifying the neglect of dissociative equilibria were presented. Experimental values of the detonation velocity were employed to calculate the covolume constant k for a series of explosives. The resulting values of k showed an overall dependence on density of 15 to 20%, an effect too great to be attributed to differences in composition of the explosion products at high and low loading densities.

The final report[11] of the series under consideration continues the development of methods for the calculation of velocities of detonation of solid explosives and contains a discussion of plane shock waves in air and water and a description of rarefaction and reflection phenomena.[c]

The more general equation of state,

$$\begin{aligned} pvM &= nRT(1 + xe^{\beta x}) \\ x &= \frac{k}{T^{\frac{1}{4}}Mv} \end{aligned} \tag{11}$$

was employed, in which the coefficient β was included in the exponential term to secure constancy of the covolume constant k with respect to density of the gases, and in which a $T^{-\frac{1}{4}}$ dependence of the covolume upon temperature was adopted. By trial, the value 0.3 was adopted for the parameter β. The rule for the composition of the products of explosion which was previously proposed was employed. A computational procedure was devised in which "ideal" values of the detonation velocity and temperature were calculated on the assumption that the product gases obeyed the ideal gas law. The correction factors resulting from the introduction of the equation of state (11) for the real gases could then be tabulated as functions of the heat capacity of the product gases, considered ideal, and the argument,

$$x_1 = \frac{\rho_1 k}{T_2^{\frac{1}{4}}M}, \tag{12}$$

where ρ_1 is the density of the intact explosive. The published tables contain a systematic numerical error which, although to some extent self-compensating, largely invalidates the values of the covolume constants evaluated by the use of experimental values of the detonation velocity. It should be noted that

[c]This reference contains all the purely theoretical material of the earlier reports by the same authors. In particular, it supersedes the discussion of plane shock waves in air and water presented by them in reference 12.

the edition of the tables employed in the evaluation of β did not contain the systematic error.

The report concludes with a discussion of shock and rarefaction waves based upon the Riemann formulation of the equation of hydrodynamics. The Rayleigh[13] solution of the Riemann equations for a simple progressive wave is given. In this case, the Riemann s is constant over a region and the r lines are therefore straight. Then

$$u = f[x - (u + c)t], \tag{13}$$

where f is an arbitrary function determined by the boundary conditions at the generating surface and the Rankine-Hugoniot conditions, equations (5), which are supernumerary boundary conditions which must be satisfied at the shock front.

Rarefaction waves are considered, and it is shown that in the case of rarefaction no discontinuity can occur. A qualitative description of the profile of a plane detonation wave is given, and it is shown that the detonation wave is followed by an advancing rarefaction wave. Tables of the peak values of the temperature, pressure, density, and shock wave velocity as functions of the peak value of the particle velocity for shock waves in air and water are presented. These are constructed with the aid of the Rankine-Hugoniot conditions, equations (5), and in the case of air, the values were taken from a report by Bethe and Teller.[14,15]

Following a discussion of reflection phenomena at boundaries, a method is developed for the calculation of the initial shock wave velocity for a shock wave initiated by a plane detonation wave. It is shown that the Riemann r must be constant across the boundary between explosion products and exterior medium. This constant becomes half of the particle velocity of the explosion products immediately behind the detonation front if the Riemann ω function for the exterior medium is defined as

$$\omega \int_{\rho_2}^{\rho} \frac{c}{\rho}\, d\rho, \tag{14}$$

where ρ_2 is the density of the gases behind the detonation front. Then

$$u_3 = -\omega + u_2\,, \tag{15}$$

where u_3 is the initial particle velocity in the exterior medium and u_2 is the particle velocity behind the detonation front. Since ω may be considered a function of p only, the initial shock pressure may be determined and the initial shock velocity follows from the Rankine-Hugoniot equations (5). A sample calculation is given for shock waves in air, employing the equation of state (11) for the explosion products and the ideal gas adiabatic equation of state for air. Numerical results are given for PETN and Tetryl, each at two loading densities. The calculated values of the initial shock wave velocity are in good agreement with experiment.

An extension of the procedure for calculating the velocities of detonation of solid explosives to include those explosives which yield solid carbon as a reaction product has been accomplished by the assumptions that the volumes of solid and gas are additive, that the gas obeys the equation of state (11), and that the solid has zero coefficients of thermal expansion and basic compression.[16] The composition of the reaction products is assumed to be that for chemical equilibrium at the temperature and pressure immediately behind the detonation wave, and a numerical procedure, involving successive approximations, is developed for the determination of this composition from a consideration of the simultaneous equilibria involved. On the basis of an assumed composition, a value of the "ideal" temperature T_2^* is found on the assumption that product gases are ideal. The correction factor T_2/T_2^* and the quantity x_2, defined by

$$x_2 = \frac{k}{T_2^{\frac{1}{4}} M (v_2 - \eta v_s)}, \tag{16}$$

(v_s and η are the specific volume and weight fraction respectively of solid C) are tabulated as functions of γ^*, the ratio of the heat capacities of the explosion products, gases being considered ideal, and the argument,

$$x_1 = \frac{\rho_1 k}{T_2^{\frac{1}{4}} M (1 - \rho_1 \eta v_s)}\,, \tag{17}$$

The specific volume of the explosion products behind the detonation front is determined by equation (16), and the pressure is then determined by the equation of state. These values of the state variables are then employed in a determination of the equilibrium composition of the explosion products by ordinary thermodynamic methods. The resulting composition is employed in a new determination of the pressure, temperature, and specific volume behind the detonation front, and the cyclical computational process is continued until successive approximations to the composition and the state variables are identical to some desired degree of precision. An "ideal" value of the detonation velocity D^* is then found on the assumption that product gases are ideal, and the correction factor D/D^* is obtained

from a table of the quantity as a function of the arguments γ^* and x_1. The particle velocity may then be evaluated from the second of the Rankine-Hugoniot conditions, equations (5).

As a consequence of the determinations of the composition at equilibrium of the products of the explosion reaction, it is shown that a good approximation to the composition is afforded by the following conventional scheme. In listing the products of the reaction, it is assumed that oxygen reacts first with hydrogen with the quantitative formation of water, the remaining oxygen reacts with carbon to form carbon monoxide, and additional oxygen, if any, reacts with carbon monoxide to form carbon dioxide. The conventional decomposition scheme suggested by Kistiakowsky and Wilson resulted from a consideration of the water-gas equilibrium in which the effect of the nonideality of the gases was not included. The effect of gas imperfections is to reverse this equilibrium completely, thus giving rise to the conventional decomposition scheme outlined above. The detonation velocity is insensitive to the composition of the explosion products, and calculations based upon the conventional decomposition scheme differ little from the much more elaborate calculations which include the determination of the equilibrium composition.

The covolume constants were determined from experimental values of the detonation velocities of selected explosives by an extensive series of successive approximations which are outlined in the report under review. The final values of the constants for the individual gas species are closely proportional to the high temperature values of the van der Waals b as evaluated by Hirschfelder, McClure, and Curtiss.[17]

The computational methods described in reference 16 have been applied to the calculation of velocity of detonation, and temperature, density, and pressure of the detonation wave front for sixteen organic explosives.[18] Comparisons of the calculated velocities of detonation with experimental values were possible with twelve of the explosives. Agreement was satisfactory for seven of the explosives; with five of the explosives the calculated values were lower than the experimental values. These five explosives have high detonation rates and relatively high oxygen contents.

In some as yet unpublished work at the Explosives Research Laboratory[19] a simplified calculation of the velocities of detonation of solid organic explosives has led to better agreement with experimental values than have the more elaborate calculations just described. In the simplified calculation the equation of state (11), with a single covolume constant per unit mass of gaseous explosion product, was employed. The conventional decomposition scheme, suggested by Brinkley and Wilson, which leads to quantitative formation of water, was employed to estimate the composition of the products. The covolume constant was evaluated by use of experimental values of the detonation velocity of oxygen-rich explosives. The specific volume of solid carbon was treated as an adjustable parameter and its value was determined by the use of experimental values of the detonation velocity of oxygen deficient explosives. The best fit between theory and experiment is obtained with a covolume constant of 12.7 per gram of gaseous product and with a value of 0.340 cc per gram for the specific volume of carbon. With these parameters, calculated and observed detonation velocities are in good agreement, i.e., better than 6%. The agreement would have been considerably improved, if nitroguanidine, an explosive with exceptionally low detonation temperature, had been given less weight in the least squaring process employed for the determination of the covolume constant.

By 1946, the best experimental values of the detonation velocity had become somewhat different from the earlier values employed by Boggs and Martin, and this would result in a somewhat different value of the covolume constant. A small residual variation in the covolume constant with density of explosive suggests that the parameter of the equation of state (11) should be re-evaluated. It is felt that the use of a $T^{-\frac{1}{3}}$ dependence of the covolume on temperature, which would necessitate the re-evaluation of both the covolume constant and β, would improve the agreement between theory and experiment for *cold* explosives without sacrificing the excellent agreement obtained by Boggs and Martin for the explosives with higher detonation temperatures.

Calculations of detonation pressures have been made and are presented in references 20 and 21.

In the former report the pressure inside aerial bombs at the instant of explosion has been calculated for several fillings, namely, Composition B, 50/50 Amatol, 60/40 Amatol, 50/50 Amatex, 60/40 Amatex, and TNT at certain initial densities reported as used in practice. Composition B gave about 20% higher values than Amatol and Amatex, which were nearly the same, while the TNT was about 15% lower than the Amatol-Amatex group. The TNT result would have been somewhat higher if its density had been nearer the others.

The above results, as well as the initial temperature, density, composition, and the calculated detonation velocity, were obtained from the hydrodynamic-thermodynamic theory previously described[16] and represent values right behind the detonation wave front. The same order applies to the values obtained on the assumption of an adiabatic constant volume explosion. An outline of both calculations is included. In the one the quantities calculated are those which occur just behind the detonation front as it travels down the length of the bomb. In the other, it is assumed that the pressure throughout the bomb has been equalized without loss of energy or expansion.

In the latter report the pressure immediately behind the detonation wave front, the detonation velocity, and the pressure of adiabatic constant volume explosion have been calculated for several service explosives at loading densities reported to be employed in aerial bombs. An estimate has been obtained of the maximum available work of each explosive. The calculations of the properties of the adiabatic constant volume explosion state assume that the pressure is equalized throughout the bomb without loss of energy or expansion.

Composition B gives significantly higher values of each of the above quantities than Ednatol, Amatol, Amatex, and TNT. The order of the other explosives is dependent on the loading density of the different fillings. When compared at the same loading density in terms of adiabatic constant volume explosion pressure or of the maximum available work, the order is Ednatol, 60/40 Amatex, 50/50 Amatex, TNT, 50/50 Amatol, 60/40 Amatol. This order may be changed by a variation of a few hundredths in the loading density. The loading density seems to be more important than the type of filling with the Amatols, Amatexes, and TNT, as far as the adiabatic constant volume explosion state is concerned.

It is further shown that surrounds of TNT equal to 7% of the total explosive have a negligible effect on the adiabatic constant volume explosion pressure of 50/50 Amatol or 50/50 Amatex.

In addition to the work described in the preceding pages, Division 8[d] also supported investigations of related problems: the theory of detonation waves[22] and a theoretical study of the initiation and propagation of detonation waves.[23,24]

[d]The final report on this work as a Division 8 project and the report on its continuation as a direct project of the Bureau of Ordnance make up a BuOrd report which has not been issued as of the closing date of this summary.

Chapter 6

PROPELLANTS

The work on propellants in Division 8 did not get under way until sometime later than the work on high explosives, and at the termination of the activities of the Division a larger part of its effort was being spent on propellants than on high explosives. One large portion of the work on propellants can be outlined in the following terms. Double-base powder has excellent mechanical properties and is smokeless. It has, however, two serious difficulties in terms of the requirements of modern war. The ballistic properties vary considerably with change in temperature, and it is not possible by solvent or solventless extrusion to prepare grains of large diameter, for example, 8 inches or more. Division 8 undertook to develop propellants which would not be subject to these two handicaps. Molded composite propellant (6.2) consists of a fuel (ammonium picrate) and an oxidant (alkali nitrate) held together by a resinous binder. A composite propellant can be made in grains of large diameter and its ballistic properties vary only slightly with the ambient temperature; it produces large amounts of smoke on burning. Cast perchlorate propellant (6.4) is a material which can be poured into a mold and cured in place. It too offers the possibility of preparing very large grains and it too produces smoke on burning. Solvent extruded composite propellants (6.3) consist of a double-base matrix and a filler which is a mixture of fuel and oxidant. Their ballistic properties are quite consistent over a considerable temperature range; but because of the filler they produce smoke and, like other double-base powders, there is a limit to the grain size. The most promising single development in this general direction was that of cast double-base powder: grains of double-base powder are treated with an explosive solvent: on warming, the grains swell and coalesce to a single large grain the size and shape of the mold. When this casting process is combined with the use of small amounts of solvent-extruded composite propellant to govern the burning rate, one has, as a result, a powder which combines the desirable features of double base and the composites.

In connection with the propellants described in the preceding paragraph theoretical studies were made of the mechanism of burning of propellants (6.1), and experimental studies of the design and construction of nozzles for use in motors burning these propellants (6.6).

Gun propellants, rather than rocket propellants, formed the subject of other lines of investigation. Flashless powder for Navy guns was developed in which the nitroglycerin of the British Cordite N formula was replaced by the explosive plasticizer DINA. By incorporating RDX and a deterrent in nitrocellulose, a start was made on the development of powder for small arms and cannon which would either have the same potential as current powder but be less erosive or would have higher potential than current powder and be no more erosive.

A large program of experimental work on double-base powder was also carried on. This included stability and surveillance measurements and studies of methods of measurement. Methods of analysis of powder were developed and studies were made of the physical properties of double-base powders as a function of their composition. These studies will be found described in detail in Sections 6.9 through 6.14.

6.1 THE THEORY OF THE BURNING OF ROCKET POWDERS[a]

6.1.1 Introduction

With the development of composite propellants (see Sections 6.2 and 6.3) it became desirable to make a theoretical study of the burning of these propellants in order to gain a better understanding of the reasons for their desirable ballistic properties and, ultimately, to be able to improve them. Before starting this study, however, it was necessary to develop somewhat further the theory of the burning of double-base powders, and actually the main part of this summary will deal with this topic. A section at the end will take up the composite propellants. The theory is based very largely on the experimental work of Dr. B. L. Crawford, Jr., and his associates at the University of Minnesota. Not only have they performed a beautiful series of experiments, both on double-base and composite propellants, but they have also made many suggestions regarding the theory. The preliminary

[a]This section is taken from a summary prepared by O. K. Rice.

calculations on the theory have been presented in a series of interim reports. Except for the last,[6] these contain some errors.[1-6] The final results are given in references 7 and 8, which also contain more complete lists of references than are given here to the work of Crawford and others.

6.1.2 Theory of Burning of Double-Base Powders

Theories heretofore proposed for the burning of propellants may be divided into two general classes. The first assumes that heat developed in the reacting gas beyond the surface of the powder is conducted back to that surface, thus affecting the rate of reaction at the surface, which is assumed to play an important role in determining the rate of burning. The second assumes that the rate of burning is determined solely by the reactions in the gas phase, conduction of heat back to the surface playing only a secondary role. The first type of theory is the main theme of the present summary, but the second, which has been developed by Boys and Corner,[9] has also been considered to some extent: in particular, a proof, which involves no integration of the differential equation, has been given of Boys and Corner's proposition that the slope of the curve, logarithm of the rate of burning against logarithm of the pressure (the pressure coefficient, an important quantity ballistically), is equal to half the order of the gas-phase reaction under the particular assumptions of their theory.

The burning of the powder appears to occur in three stages, all with evolution of heat. The first stage occurs at the surface of, or within, the solid powder and results in the formation of unsaturated fragments which are ejected into the gas phase normal to the surface. In the second stage, these fragments react in the gas phase in an assumed second-order reaction. These two stages together constitute the fizz burning; the gases produced are still capable of further reaction. At low pressures (from one to a few atmospheres) the only heat reaching the surface is that produced by the reaction at the surface, which is thus self-sustaining at a definite (limiting low-pressure) rate. (At still lower pressures the rate drops again; this phenomenon is not treated in this summary.) At higher pressures heat generated from the gas-phase reaction can reach the surface and the reaction rate then increases with pressure.

The third stage of the reaction consists of the flame, which appears only at pressures exceeding 20 atmospheres, and apparently does not affect the rate of reaction until the pressure reaches about 100 atmospheres. The flame reaction is assumed to be of the nature of a branching-chain explosion; this is supported by its appearance. It is supposed that after the gases leave the fizz zone there is built up a small concentration of active particles, this occurring in the dark zone which is observed between the surface of the powder and the flame. When these active particles reach a sufficient (but still exceedingly small) concentration an explosion occurs, which lasts through a small but definite zone at the base of the flame.

This picture of the burning process is summarized and the notation established in Figure 1.

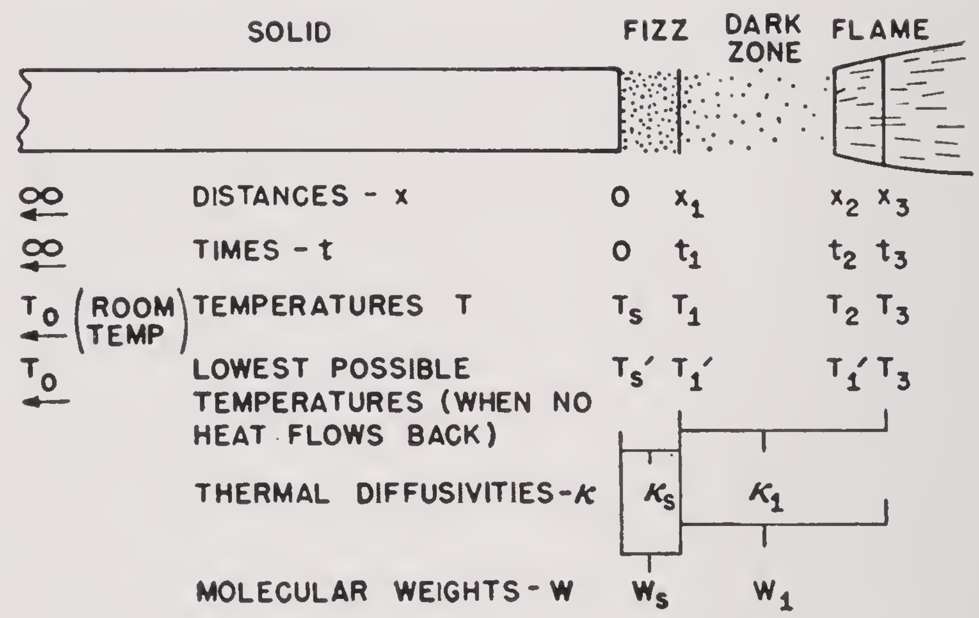

FIGURE 1. Schematic sketch of a stick of burning powder.

When a steady state is established, the total amount of heat which crosses any cross section of the powder or the reacting gas (the sum of that carried by conduction and that carried by mass motion) must be the same for all cross sections. This "law of steady heat flow," which is of fundamental importance in the theory, was established by Boys and Corner and independently by J. E. Mayer in unpublished work.

Transfer of Heat to the Solid Surface in Fizz Burning

Coming to the details, we first consider the fizz burning process, neglecting the effect of the flame. Applying the law of steady heat flow to the problem of conduction of heat from the exothermically reacting gas back to the surface, but assuming that all the reaction in the gas takes place in a single plane at x_1, there may be derived a fundamental relationship, which connects the pressure p, the burning rate M, and the temperature of the surface T_s:

$$p = \frac{MRT_s}{W_s z_1}\sqrt{\frac{t_1}{\kappa_s}}\,, \tag{1}$$

where

$$z_1^2 = \ln \frac{T_1 - T_s'}{T_s - T_s'}\,. \tag{2}$$

M can be expressed in the form of an Arrhenius equation,

$$M = Ae^{-E_s/RT_s}, \tag{3}$$

where A is a "frequency factor" and E_s the energy of activation of the reaction that takes place at the surface of the solid. Since W_s, t_1, κ_s, T_s', T_2, E_s, and A are to be considered as parameters, values of which are to be preassigned, T_s and z_1 can be eliminated from these equations, to give M as a function of p, obtaining a curve which can be compared with experiment. The equations can be easily generalized to take care of the fact that the reaction in the gas takes place over a finite zone instead of in a single plane. This effectively simply replaces equation (2) by another relation.

In eliminating T_s and z_1 from the equations, it is assumed that t_1 is given by

$$t_1 = \frac{1}{k_1 p}, \tag{4}$$

where k_1 is a rate constant independent of the temperature; that is, the activation energy of the gas-phase reaction is negligibly small. If this reaction had a high activation energy, t_1, the time required before reaction occurs after the fragments leave the surface, would not depend primarily on a rate of reaction, but on how long it takes the gas to move out to a point where it is hot enough to react, and the theory would revert to the Boys-Corner type, which makes the slope of the log M versus log p curve equal to just half the order of the gas-phase reaction. If this energy of activation is low, t_1 is the time of reaction after the fragments leave the surface, the theory developed in this summary will apply, and other factors as well as the order of reaction will affect the slope of the curve. Certain characteristics of the burning rate versus pressure curve and related effects offer evidence to show that the latter alternative is correct.

If we are interested only in the burning rate at moderately low pressures, the above equations are all that are needed. Temperature and pressure coefficients for the fizz burning region are readily derived. The pressure coefficient turns out to be largely determined by the ratio M_1'/M_s', where M_1' is the value of M at the temperature T_1' attained by the gaseous products of fizz burning if there is no flame, and M_s' is the value of M at the lowest possible (low-pressure) value T_s' of T_s. Under these circumstances, of course, $T_1 = T_1'$; otherwise T_1 is determined by the flame.

Effect of the Flame on the Burning Process

This is important at higher pressures, above about 100 atmospheres. It is first necessary to consider the nature of the branching-chain reaction and to attempt to correlate it with the measurements on the length of the dark zone as a function of pressure made by Crawford and his collaborators. We assume that the flame starts when certain active constituents, which are formed in the gas starting from the end of the fizz zone, reach a certain critical concentration. The rate at which these active particles are formed will depend on the pressure (but not, at least greatly, on the temperature), and the critical concentration may also depend on the pressure. If we let c_2 be the concentration of active particles, we have

$$\frac{dc_2}{dt} = k_2 p^{n_2}, \tag{5}$$

where k_2 is a rate constant and n_2 the order of the reaction. If the critical concentration of c_2 is of the form B/p^m, where B and m are constants, then the time (after the time t_1) necessary for the development of the critical concentration and, hence, for the flame to start, is

$$t_2 - t_1 = \frac{B}{k_2 p^{m+n_2}}. \tag{6}$$

The distance $x_2 - x_1$, which is essentially the length of the dark zone, since $x_1 \ll x_2$, can be shown to be given by

$$x_2 - x_1 = \frac{KT_1 M}{p^{m+n_2+1}}, \tag{7}$$

where

$$K = \frac{RB}{W_1 k_2}. \tag{8}$$

To get agreement with the earlier measurements of Crawford, Huggett, and Parr[10a] one would set $m + n_2 + 1 = 3.5$, but later experiments[10b] indicate a larger value; we have taken, in later work, 5.5.

For this dark zone we get an equation analogous to equation (1):

$$p = \frac{MRT_1}{W_1 z_2}\sqrt{\frac{t_2 - t_1}{\kappa_1}}, \tag{9}$$

where

$$z_2^2 = \ln \frac{T_2 - T_1'}{T_1 - T_1}. \tag{10}$$

Finally, we have to consider the reaction taking place in the finite reaction zone (x_2 to x_3) in the flame. It is this zone in which the heat of the flame

reaction is actually generated, only a small concentration of active particles being built up in the dark zone. Also we must suppose, in order to get any agreement with the rate-pressure curve, that the reaction zone in the flame does not have nearly so high a dependence on pressure as the dark zone, so that the reaction zone actually is much longer than the dark zone at sufficiently high pressures. We assume, in fact that

$$t_3 - t_2 = \frac{1}{k_3 p}, \tag{11}$$

where k_3 is a constant. We can write another equation analogous to equation (1):

$$p = \frac{MRT_1}{W_1 z_3}\sqrt{\frac{t_3 - t_2}{\kappa_1}}, \tag{12}$$

where

$$z_3^2 = \ln \frac{T_3 - T_1'}{T_2 - T_1'}. \tag{13}$$

To take care of the finite reaction zone, we would again replace equation (13) by another relation.

It is now possible, if the parameters are known, to handle equations (1) to (4) with equations (6) to (13) simultaneously, eliminating unnecessary quantities and obtaining a relation between M and p which will hold into the pressure region above 100 atmospheres.

Equation of the Parameters

Before the equations of the preceding sections can be applied, various parameters must be determined. Estimates of the important quantities for a typical double-base powder (HES 4016) are herewith tabulated.

$T_s' = 770$ K	$\kappa_s = 0.6/p$, cm²/sec, (p in at.) at 770 K
$T_1' = 1100$ K	$\kappa_1 = 2.8/p$, cm²/sec, (p in at.) at 1100 K
$T_3 = 3000$ K	$\kappa = 49$ at.$^{3.5}$ cm³ sec/g deg if $m + n_2 + 1 = 3.5$
$W_s = 57$g/mole	$\kappa = 9\text{x}10^4$ at.$^{5.5}$ cm³ sec/g deg if $m + n_2 + 1 = 5.5$
$W_1 = 27$g/mole	$E_s = 17{,}300$ cal per mole reaction

Mostly these are based on data obtained by Crawford and his collaborators, but T_s' is a guess limited by the fact that an opaque double-base powder shows no red glow while fizz burning, and $T_1' - T_s'$ is obtained from the experimental temperature coefficient. This temperature difference is important in the theory, and is rather definitely fixed by the temperature coefficient. E_s depends upon T_1' and T_s' and on M_1' and M_s'. The latter are in turn so chosen as to best fit the burning rate data, as are k_1 and k_3. These quantities are not given here, but k_1 will be discussed below.

The Burning Rate-Pressure Curve

The experimental curve for log M versus log p shows, in general, a flat region or at least one of small slope at low pressures. This corresponds to the region where T_s is close to T_s'. In the higher pressure range, where heat is getting back to the surface from the gas phase, the slope of the log M versus log p curve rises gradually, eventually approaching about 0.7. This general trend is very well reproduced by the theory.

In some types of powder, the curve tends to flatten out again at pressures around 100 atmospheres, to be followed by a rather noticeable rise where M begins to go up because heat from the flame reaction begins to reach the powder in appreciable quantities (S-shaped curves). In the usual type of double-base powder, such as HES 4016, there is no such marked effect of the flame, but a pretty good idea of the pressure at which the flame begins to be effective may be obtained by comparison with a similar powder in which catalyzed nitrocellulose was used.[10c] With this powder the flame is much closer to the surface than with ordinary HES 4016, and the rate of burning is higher at high pressures but about the same at low pressures. To get the effect of the flame to come in at a sufficiently low pressure it appeared necessary, if $m + n_2 + 1 = 3.5$, to assume that κ_1 was actually about 20 times as large as that tabulated above. However, later it was found that with $m + n_2 + 1 = 5.5$ and the flame consequently approaching the surface much more rapidly, the discrepancy was reduced to 4- or 5-fold, and it was concluded that this was within the limits of error.

Effect of Coolants

The effects of added coolants, such as centralite and paraformaldehyde,[10d] on the parameters can be estimated. Since these coolants can be assumed to be either inert ingredients which do not take part in the reaction (centralite) or substances which actually decompose and absorb heat in the solid phase (paraformaldehyde), the effect is to lower T_s', T_1' and T_3. Reasonably good, though not absolutely accurate, predictions of the effect of the coolants can be made. Especially interesting is the case of a 20% paraformaldehyde powder. The predicted curve shows a very low rate in the fizz burning region, with a very steep rise where the flame comes in. Actually, the powder will not burn in the low pressure fizz burning region, but the points at higher pressures fall near the curve in the region where the flame has a pre-

dominating effect. Other types of coolant exist, which cool the flame and produce the S-shaped curves noted above.

Reaction Times and Distances and Their Interpretation

A question arises as to whether the solid-phase reaction actually occurs at the surface, or whether it takes place in a finite region within the solid. In favor of the first hypothesis are the facts (1) that the value of A corresponding to the estimated values of M_1' and M_g' is close to what one might expect from a unimolecular decomposition of the exposed NO_3 groups, and (2) that microscopic examination of the surface of powder which has been burned and quenched shows an altered layer, which, if the quenching occurred at 150 psi, is about equal to the thickness which one might expect to be heated by conduction.[11] In favor of the second hypothesis are the facts (1) that if the quenching occurs at atmospheric pressure the altered layer is much larger than expected.[12] and (2) that the altered layer is full of bubbles.[10e] It seems certain that there is a reaction within the solid, but it may not be important except at low pressures.

The value of k_1 which must be used to get agreement with the burning-rate data is only about 1.7×10^{-6} times as great as would be the case if the gas-phase reaction took place at every collision of the reactive fragments. However, there is undoubtedly a small, rather than actually zero, activation energy, which accounts for this factor in part.

It may be noted that the length of the fizz zone can be calculated, though there are no experimental data for comparison. Some values of this length, x_1, at various pressures, are as follows:

p (at.)	1.66	7.3	29.	160.
x_1 (μ)	334	35	5.2	0.63

Relationship with Other Work and Suggestions for New Work on Double-Base Powders

In the theory considered above, nothing was said in explanation of the rather sharp falling off of the rate at very low pressures (below 1 atmosphere). A start on a theory of this effect has been made by Crawford and Parr.[10f]

The theory considered here assumes that the activation energy of the gas-phase reaction is low, though the possible errors caused by the assumption have been discussed a little. The work of Boys and Corner assumes it is high. A start at working out the intermediate case has been made by Parr (reference 10g and private communications).

Shortly after this theory was developed in the RP reports, an essentially equivalent theory, though differing greatly in mathematical details, was worked out by Eyring and his co-workers[13-14] for the fizz burning. Their application, however, contained an error. They did not consider the effect of the flame on the burning rate but did consider the possible effect on the flame of the diffusion to the side. In this way they attempted to explain the dependence of the dark-zone length on pressure, assuming an ordinary second-order reaction in the flame. In these calculations, however, they apparently overlooked the dependence of the diffusion constant on pressure, and, in any event, the experiments at the University of Minnesota indicated that diffusion is probably not important except at rather low pressures.

One of the chief desiderata in the further study of double-base powders is some more accurate way of estimating the temperature of the surface of the burning powder. The method used by Daniels, of incorporating in the powder substances which melt or decompose at definite temperatures, is not unequivocal, for one reason because the particles of the substance may stick out into the gas and be heated there. Possibly, use of a larger variety of smaller particles would be helpful. Other methods[15] have also been used but do not give unequivocal results.

At the present stage of our knowledge of double-base powders, it seems that detailed examination of powders with special properties, e.g., the paraformaldehyde powders, along the lines so well outlined by Crawford and his associates would be helpful. For example, further burning rate data on various intermediate compositions of paraformaldehyde powder, examination of the burned surface, analysis of products, heat of explosion data at various pressures, dark zone data, and the effect of using catalyzed nitrocellulose in such a powder, would be interesting and theoretically significant.

6.1.3 The Theory of the Burning of Composite Propellants

Use of the principles laid down above and the very excellent experimental work at the University of Minnesota (references 10h and 10i and various private communications and memoranda) have made it possible to attempt some speculations on the burning of composite propellants, which contain a filler of the

oxidizing agent potassium perchlorate and the reducing agent, carbon black, in a binder of double-base powder. The perchlorate particles are of the order of 7.5 μ in diameter, while the particles of carbon are much smaller, around 0.03 μ.

The theory is based upon a consideration of what happens to individual perchlorate particles. When a powder containing very little filler is burned, individual perchlorate particles can be seen glowing in the surface, and they evidently have a higher temperature than the rest of the powder. According to Crawford, Huggett, McBrady, and Hanson, only the larger perchlorate particles glow. Some of them give rise to plumes of flame, presumably due to reaction of oxygen from the particles with reducing gases and carbon from the surrounding powder. Of course, in a powder containing more filler, the plumes of flame are merged to give an apparently uniform flame. A large crystal embedded in double-base powder also gives rise to a flame, and from the rate at which the crystal is consumed and the known rate of decomposition of potassium perchlorate at various temperatures, its surface temperature can be estimated to be considerably higher than that of the surrounding powder.

As regards the burning rate, the experimental facts are roughly as follows: At sufficiently low pressures the perchlorate lowers the rate of burning. There is then a very sharp rise in the burning rate, around 100 psi (the higher the percentage of filler, the lower the pressure at which this occurs), after which the rate increases only moderately with pressure, so that in the ballistic region the powder shows the desirable low pressure coefficient. A more finely ground perchlorate gives, apparently, a lower rate at low pressures and certainly a higher rate at high pressures.

The theory which accounts for or describes these facts may now be outlined. At very low pressures, where it lowers the rate, the perchlorate is supposed to act as an inert ingredient. (Actually there is some question whether it lowers the rate as much as it should on this basis.) But there is a tendency for it to react at the surface with gases from the binder. At somewhat higher pressures this reaction may become important, causing the particles to be heated above the temperature of the binder. It is possible that only the larger particles, which stick through the fizz zone, are thus heated; this would also result in dependence on the pressure, since the thickness of the fizz zone decreases sharply with the pressure. Having been thus heated, some of the particles emit sufficient oxygen so that the plumes of flame burst from them. When this happens more heat is generated, the surface is heated more strongly, and the effect is likely to be contagious, especially in a powder of high filler content, so that more particles burst into flame. As the pressure increases, more and more particles burst into flame; in view of the remarks just made, this effect is autocatalytic, so that there is a region around 50 to 100 psi where there is a sharp rise of rate with pressure. At somewhat higher pressures, however, where practically all of the particles burst into flame, this effect reaches saturation; only the normal tendency for the rate of burning to increase with pressure remains, and the rate of reaction of the gases becomes determined largely by diffusion of the oxygen and the reducing materials into each other. Under these circumstances increase in burning rate is resisted by the diffusion process, and the pressure index goes down below the normal values.

The smaller the perchlorate particles the easier is diffusion around them, accounting for the effect of size in the high-pressure region. At low pressures, decreasing the size of the perchlorate particles may result in their being more uniformly heated throughout their bulk. Thus a given weight of perchlorate would, if finely divided, act as a better cooling agent, causing the powder to burn slower.

The carbon black, whose effect has not been discussed so far, plays an important role in the combustion. It may act as a catalyst, or it may act as a concentrated reducing agent carried in the reducing gases which react with the oxygen from the perchlorate. In either case, absence of carbon would be expected to cause partial repression of the steep rise of rate with pressure at 100 psi, causing this increase to occur instead in the ballistic region. This prediction has since been confirmed by experiment.[16]

Suggestions for Further Work on Composite Propellants

1. The decomposition of potassium perchlorate should be more thoroughly studied.

2. Controlled reaction rate experiments between potassium perchlorate and gases, such as are given off in fizz burning of double-base powders, might be of interest.

3. A careful study of the effect on the burning rate of the size of the filler particles at low pressures as well as at high pressures should be made. Some work of this nature is already under way.

4. Some light on the effect of an inert ingredient at low pressures might be obtained by experiments using

a nonreactive material such as powdered sand, varying the particle size and percentage of sand.

5. Photographs should be made (like those made by Crawford, Huggett, McBrady, and Hanson for powders dilute in filler) of powders with high filler content around the pressures at which the sharp rise in rate just begins, to see if the inflammation of perchlorate particles can be detected and studied.

6. Photographic studies should be made of powders containing very little potassium perchlorate and varying amounts of carbon black.

7. Estimates should be made of the smallest size of perchlorate particle which glows (compare Crawford, Huggett, McBrady, and Hanson) when a dilute powder burns under varying pressure conditions, to see whether this size parallels the thickness of the fizz zone. If this is found to be the case, it might indicate that the particles are heated and glow only if they stick up into the hotter regions of the gases.

8. Powders in which the perchlorate is replaced by a solid solution of potassium perchlorate and potassium permanganate might be studied, if stability tests indicate that they can be used. Since these solutions decompose more readily than pure potassium perchlorate, some light might thereby be thrown on the effect of the stability of the oxidizing agent.

9. Some consideration should be given to the effect of the size of the carbon particles. Since a large carbon particle might not react completely with the oxygen from the potassium perchlorate, at least close to the surface, and since, with its relatively smaller surface it would be a poorer catalyst, it might be expected that increasing the size of the carbon particles would have the same effect as decreasing their concentration.

6.2 MOLDED COMPOSITE PROPELLANTS[b]

Molded composite propellants are mixtures of finely divided, crystalline, self-combustible solids, for example, ammonium picrate and sodium nitrate, held together by a resinous binder and formed into grains by compression molding. The development of these propellants[17] had its origin in observations made by British workers prior to the summer of 1941. The British effort, however, was directed primarily toward the preparation of plastic propellants, puttylike materials which would be molded directly into rocket motors, whereas the work of Division 8 was directed toward the preparation of hard, mechanically strong grains.[c]

Molded composite propellants possess certain major advantages over conventional propellants.[19-21] They have a low value of the exponent in the burning law, which results in a much lower sensitivity of the pressure in a rocket motor to such influences as changes in burning surface, nozzle area, limited area of passages for flow of gas, than is the case with ordinary double-base powders.[d] This permits packing more propellant in a given space, lightens the motors because of greater reproducibility of pressure, and compensates completely for the somewhat lower specific impulse. The propellant burns well at low motor pressure of from 200 to 800 psi. This also aids in lightening the motors. The temperature coefficient of pressure, thrust, and burning time is low so that these quantities vary over the range from —40 to +140 F by a factor of 1.5 compared with 5 for ballistite and cordite. This is extremely important for launching units and missile propulsion units, for which thrust and burning time must be as nearly as possible independent of temperature. For artillery rockets the low coefficient removes the necessity of a range correction for temperature and contributes to lower motor weight and generally increased efficiency of the projectile. The powder is mechanically strong and, although it is somewhat brittle, can easily be mounted in a motor so that the powder grain is not ruptured by impacts that will injure the metal parts of the motor. The propellants are of inherently great stability and are not altered by long storage at elevated temperatures. It is relatively easy to apply a coating to the propellant to prevent the burning of a given surface. This permits fabrication, for example, of end-burning solid charges with long burning times. A range of propellants of widely different burning rates can be obtained by simple changes of propellant composition. Thus CP-492 has a burning rate of 1.0 in. per second at 1,000 psi and 70 F, whereas CP-401 has a burning rate of only 0.24 in. per second under the same conditions. This flexibility contributes ad-

[b]This section is constructed from a summary prepared by Louis P. Hammett and Frank A. Long.

[c]The work done by Division 8 on plastic propellants differed from that of the British in that a thermosetting rather than a thermoplastic binder was used, and the binder was incorporated in edge-runner mills rather than in differential rolls. Not enough work was done by Division 8 to develop a plastic propellant satisfactory in every respect, but sufficient work was done to show the great potentialities of this type of propellant.[18]

[d]Persons not familiar with these and other terms used in connection with rocket propellants will find an excellent introduction to the subject in reference 22.

ditional latitude in the design of propulsion units. Finally the propellants are exceedingly well adapted to production in charges of relatively large diameter. Under wartime conditions the fact that the major components, potassium nitrate and ammonium picrate, were in good supply was an additional favorable factor.

The compositions and properties of several of the standard composite propellants are given in Table 1.

TABLE 1. Composition and ballistic properties of molded composite propellants.

Designation	218B	401	404	492
Ammonium picrate	46.7	72	54.0	41
Sodium nitrate	46.7	...	...	...
Potassium nitrate	...	18	36.0	50
Buramine resin*	5.1	...	...	...
Santicizer 8†	1.5	...	...	...
Calcium stearate	0.4	...	...	...
Ethylcellulose‡	...	4	5.0	4.5
Aroclor 1254§	...	6	5.0	4.5
I	172	174	174	165
d	1.80	1.64	1.72	1.77
I_d	310	285	300	292
n	0.50	0.50	0.45	0.42
$R_{1,000}$	0.70	0.24	0.57	1.0
$K_{1,000}$	170	600	240	155
Temp coef	0.005	0.005	0.005	0.003

I, the specific impulse in seconds, is given for a chamber pressure of 1,000 psi, and the optimum expansion ratio for that pressure. The value under other conditions may be estimated from the curves in Explosives Research Laboratory Report OSRD-1627, July 1943, or from the California Institute of Technology Report CIT/JAC 2, October 23, 1942. As shown in OSRD-1627 and 5043, the ratio of the specific impulses of two propellants is essentially independent of pressure and expansion ratio except under conditions of overexpansion. Because of the greater heat losses with small motors, the specific impulse is affected by motor size and is about 9% lower for 1-ounce grains of 218B than for 4.5-lb grains.

d is density in g/cc.

I_d is the impulse per unit volume of propellant (g sec/cc).

n is the exponent in the burning law, $R = bP^n$.

$R_{1,000}$ is the linear burning rate (in./sec) at a pressure of 1,000 psi and at 25 C. Rates at other pressures and temperatures may be calculated from the values of exponent and temperature coefficient listed.

$K_{1,000}$ is the ratio of burning surface to nozzle throat area (the restriction coefficient) at which a steady-state pressure of 1,000 psi is attained. Values for other pressures may be obtained from the equation

$$\frac{P}{1{,}000} = \frac{K}{K_{1,000}} \cdot \frac{1}{1-n}.$$

The temperature coefficient is the quantity

$$\frac{1}{P}\frac{(\partial P)}{(\partial T)_K} = \frac{1}{R}\frac{(\partial R)}{(\partial T)_K},$$

in which K is the restriction coefficient.

*Buramine is a butyl urea-formaldehyde resin manufactured by the Sharples Solvent Company. It is employed as a 65% solution in butanol.

†Santicizer 8 is a trademarked plasticizer made by the Monsanto Chemical Company.

‡The ethylcellulose has the following properties: standard ethoxy content; 7 cp viscosity.

§Aroclor 1254 is a liquid chlorinated polyphenyl manufactured by the Monsanto Chemical Company.

The burning rate varies considerably with composition, but the specific impulse, discharge coefficient, and exponent n are almost the same for the compositions listed. The flame temperatures are not known precisely but that of even the "hottest" composition (CP-492) is probably under 2500 K. All the compositions produce considerable smoke, primarily potassium or sodium carbonate.

The general process for the production of composite propellants[23-28] involves the addition of suitable proportions of ammonium picrate and of potassium nitrate, which has been ground to a particle size[e] dependent on the rate of burning desired, together with a 50% solution of the resinous binder in acetone to a 3-ft edge-runner mill. The 55-lb batch is milled for three hours under careful temperature control and with a current of dry air passing through the mill to remove the acetone. At the end of milling a small proportion of calcium stearate or other free-flow agent is added. The product is a solvent-free, free-flowing powder. In the pilot plant, 40 batches of this powder are blended together to give a 2,000-lb lot. This powder is thermostatted to 35 C and fed to a compression molding press. For the production of 8.5-in. diameter grains, this press may be a 425-ton press equipped with a cylindrical mold about 24 in. long provided with a core rod if a perforation is desired. Because of friction against the walls, these molding powders do not give satisfactory results if the length of the final grain is much greater than its diameter. The molding pressure is of the order of 14,000 psi, varying somewhat with the composition of the propellant. Grains are molded to have a density of about 96% of the theoretical fully packed density. The singlet grains produced are ejected from the mold, annealed for 48 hours at 60 C and inspected. During the annealing, small volume changes occur and stresses are relieved. The product is hard and strong with a compression strength of the order of 3,000 psi. The grain walls are very close to true cylinders and the ends are essentially flat and parallel. No ignition of the propellant during the molding process has occurred at any time during the whole development. Although proper control of composition, water content, temperature conditioning, and molding cycle yields grains of consistently good quality, failure of control can result in internal cracks which may lead to disastrously high pressures when the powder is

[e] A method of determining particle size is reported in reference 29; this should be compared with an earlier report, reference 30.

burned. Fortunately, an ultrasonic transmission technique has been developed which can be carried out as a routine inspection operation and which detects such flaws with a high degree of reliability.[31]

Experimental work on the improvement of this process was actively proceeding at the termination of hostilities, and some of the partially tested developments have considerable promise. Of particular interest are alternate milling methods which might both improve the quality and lower the cost, and modifications in the molding procedure which might eliminate the need for expensive, high-capacity presses.[32-34]

For many purposes a grain longer than the singlet unit is desired and is obtained by cementing the units together. This is relatively easy with perforated grains in which the direction of the burning is radial and hence parallel to the cement joints. An alkyd resin cement, General Electric Glyptal 1201, has proven completely satisfactory. With large diameter grains, a $\frac{1}{16}$-in. thick cork washer is cemented between the units to take up irregularities in the grain ends and give the assembly slight flexibility. Cork washers which are cemented on the ends of the assembled charge serve both to prevent burning on the ends, which results in more nearly neutral burning, and to cushion the mounted grain against shock. Five cork strips are cemented longitudinally on the outside of the grain to space it from the motor wall and to provide shock protection. Protection against shock by these cork mountings is completely satisfactory.

The cementing problem is more difficult with solid grains, in which the burning proceeds in an axial direction and must therefore traverse the cement joints. The cement must be a very fluid one which can be squeezed out to give a very thin yet continuous layer, and then hardened by heat or chemical action. The grain ends must be very flat to obtain a satisfactorily thin cement layer. With $8\frac{1}{2}$-in. grains, flat ends have been obtained by machining them in an ordinary metal-working lathe. A suitable cement is General Electric Permafil 2851. The results obtained when it is used with machined grains are satisfactorily reliable. Cementing problems and techniques have been described in detail.[23]

To give end burning, a solid charge of this sort must be "restricted" to prevent burning except on one end surface.[24] This has been satisfactorily accomplished by first spraying the surfaces to be restricted with a Glyptal lacquer followed by the application of an industrial tape or by shrinking on a thin rubber tube. Here also cork sheeting is used to support the grain in the motor and to give it the necessary protection against shocks.

The development of the production techniques described in the preceding paragraphs is the result of extensive experimentation which was begun late in 1941. By the spring of 1942 it had been found possible to produce satisfactory composite propellants in the laboratory. The advantages of the propellants were so obvious that the recommendation was made to establish a pilot plant which would permit a study of production methods and would allow experimentation with the product on a sufficient scale to test its reliability. In view of the wartime urgency, the decision was made to build a plant of sufficient capacity (500 lb per eight-hour shift) to permit the use of production-size equipment and to have an output which might itself have some use in Service applications. This plant came into operation about the end of December 1942. The pilot plant development was slower than had been hoped, and somewhat over a year was required to demonstrate that a product of thoroughly reliable properties could be obtained under economically feasible conditions. This was partly because the process was a completely novel one, involving operations whose nature was not fully understood and for which suitable methods of control could only be evolved by much investigation, and partly because of the occurrence of a series of violent explosions in the milling operation which destroyed the mills and occasioned serious delays. Investigation showed that with a smaller batch size an ignition in the mill led to no serious damage, and the 6-ft mills with a several hundred pound batch for which the plant was originally designed were replaced by 3-ft mills whose operation has been completely satisfactory. The pilot plant studies during this period were almost exclusively concerned with a $2\frac{5}{8}$-in. diameter, perforated grain intended for artillery rocket applications and upon the 218B composition whose formula is given in Table 1. By the end of 1943, a completely satisfactory product for this purpose was being produced, and the process and quality of the product had been fully demonstrated. Early in 1944 a change was made in the study of the production of 8.5-in. and larger diameter charges, the practicability of which had meanwhile been indicated by experiments at the Explosives Research Laboratory.[38]

At the same time changes in composition resulting from investigations at ERL were made. Potassium nitrate was substituted for sodium nitrate because of the great hygroscopicity of the latter, and an entirely

new type of resinous binder was introduced. The early experimentation had proceeded from the quite obvious supposition that sufficient fluidity during the molding process and sufficient rigidity in the final product could only be combined if a thermosetting resin is used which is hardened by chemical action after the molding takes place. A thermosetting butylurea-formaldehyde resin, known as Buramine, was consequently employed as a binder during the earlier development. It was, however, discovered that this supposition is quite unjustified, and that ample strength and rigidity in the final product can be combined with ease of molding without any such hardening process, provided a resin of suitable properties is chosen.[39]

A binder composed of a highly plasticized ethylcellulose was found to give as high compression strength as the Buramine, and to yield a product of considerably less brittleness and greater resistance to sudden changes in temperature. It was further found that material with a binder of ethylcellulose plasticized by Aroclor 1254 could be milled until the content of volatile solvents had been reduced essentially to zero to yield a powder which retains sufficient flow for satisfactory molding. With Buramine, by contrast, satisfactory flow depended on the presence in the molding powder of a content of butyl alcohol lying within a narrow and difficultly controllable range; the removal of butyl alcohol after molding, without deterioration in the quality of the molded grain, was extremely difficult. For these reasons all recent production of composite propellants has used binders of the ethylcellulose-Aroclor type. There are indications that still better binders may be based upon rubbery materials, and that the use of such rubbery binders may be needed if grains of 12 in. in diameter or greater are to have sufficient resistance to fracture from very rapid and large changes in temperature.[40]

As a result of the interest of the Air Forces in large charges for jet-propulsion devices and the report of a special OSRD committee, funds were appropriated in March 1944 for the expansion of the Monsanto pilot plant and its conversion to the production of 8.5-in. grains. Temporarily the actual molding process was carried on at the Explosives Research Laboratory where a press happened to be available. The highest priority was initially given to a development of a 250-lb thrust, 50-second burning-time unit requiring a cemented aggregate of three single grains of CP-401, each 8.5 in. in diameter and 7.5 in. long, restricted to burn from one end only. By July 1944, it was possible to carry out a successful flight test at Tonopah, Nevada, in which two of these units were attached to a guided missile launched from an airplane. Performance was satisfactory and the missile was given a speed in excess of 400 miles per hour.

Further development in this direction, however, was almost completely stopped for a period of many months, because the Air Forces gave the highest possible priority to a development of a unit for launching the JB-2 bomb, the American copy of the German "buzz bomb." For this purpose the charge consists of a perforated cylinder, 8.5-in. outside diameter, 2.5-in. inside diameter and 36.5 in. long, weighing 120 lb. This develops at 70 F a thrust of 11,000 lb for a period of 1.85 seconds.[41,42] Four of these charges, each encased in a suitable motor, are attached to a launching sled, which, as initially planned, ran on a heavy nonportable rail system 400 ft long. By an ingenious development of the Air Forces, the bomb, sled, and rocket motors are converted to what amounts to a free flight rocket. This is launched from a ramp only 40 ft long and so light that the whole launching system can be permanently attached to a motor-drawn trailer or mounted on a relatively small boat. This light, highly portable launching system is a great advance over the heavy and rigid German launchers and various adaptations of those launchers which have been studied in this country.

Some 200 experimental launchings by this method had been made at the close of hostilities, with powder produced at the Monsanto pilot plant, with some assistance from ERL. Rocket performance had been demonstrated to have a high degree of reliability and the whole launching technique was in a satisfactory state of development.

The JB-2 bomb did not come into combat use, although a requirement for 500 launching units a month existed at the end of hostilities, and the construction in Texas of a production plant with a capacity of 600,000 lb of propellant a month (sufficient for 1,200 launchings) was well on toward completion. This was to be operated by the Monsanto Chemical Company under an Army Ordnance Department contract. Interest in the material remains sufficiently large so that the Monsanto pilot plant has been converted to a small production plant with a capacity of 75,000 lb per month for peacetime operation by the Ordnance Department.

With the decision to construct the production plant in Texas, pilot plant studies and the development of

control techniques for the operation of the production plant became an added responsibility of the Monsanto pilot plant. At the same time other charges of composite propellant were in various stages of development.[21,25,40,43] Two types of units had been successfully but less extensively tested in the weapons for which they were adapted. In one, intended for the propulsion of guided missiles, an 8.5-in. diameter solid cylinder 23 in. long, weighing 82 lb, treated so that it burns from one end only, develops a thrust of 250 lb over a period of 48 seconds. A modification of this contained a longer charge burning for 65 seconds, plus a booster charge consisting of an 8.5 x 15-in. perforated grain to give a high initial acceleration.[44] In the other type, the *decipede*, ten individual 8.5-in. diameter, 8.5-in. long cylinders, burning from one end only in a motor provided with multiple nozzles, develop a 1,000-lb thrust for 43 seconds. This unit is designed to propel, over the surface of the water, a demolition device for amphibious operations called the Snake. The decipede was developed under high pressure and was scheduled for use in the landings on Japan.[45]

The pressure for immediate development of usable jet-propulsion units has led to the neglect of much fundamental research and of many interesting but longer-range possibilities for improvement of these units. Recommendations for future work are given in many of the Monsanto reports cited in this section and specifically in reference 34.

For complete information about the properties, manufacture, testing, and uses of molded composite propellants, see references 46 to 64.

6.3 SOLVENT-EXTRUDED[65,71] COMPOSITE PROPELLANTS[f]

The development of solvent-extruded composite propellants grew out of the experience of the Explosives Research Laboratory with molded composite propellants. These latter materials had most desirable ballistic properties, i.e., a low pressure exponent and a low temperature coefficient, but they were not adaptable to the manufacture of long small-web grains of the type used in Army-designed rockets such as the 4.5-in. and the Bazooka; and their brittleness was a disadvantage, especially in small sizes. Furthermore, no plants existed which could be easily adapted to their production. Solvent-extruded double-base powder has less satisfactory ballistic properties, i.e., an unpleasantly large pressure exponent and temperature coefficient, but it is tough and particularly adaptable to the manufacture of the long small-web grains needed for the rockets in question. Further, there was large plant capacity available for its production. It seemed worth while, therefore, to attempt to combine the advantages of molded composites and solvent-extruded powders in a single powder containing a mixture of powdered oxidizing and oxidizable particles in a matrix of double-base powder, the latter being present in large enough proportion to permit fabrication by the solvent extrusion method. Research was started at the Explosives Research Laboratory in August 1943, and by October the desired result had been obtained on a small laboratory scale in what was called EJA powder, which contains potassium perchlorate as a principal ingredient. Its composition and its excellent ballistic properties are listed in Table 2. Its fabrication required only equipment available in large amounts in existing plants. Since the Bruceton laboratory could produce only relatively small batches of thin web powder, development was transferred to the Radford Development Department of the Hercules Powder Company. Although the value of the powder for the 4.5-in. rocket had been well demonstrated, methods for the production of material of reliable and reproducible quality had not been developed, when, in June 1944, the use of this rocket was dropped by the Air Forces, its largest potential user.

Meanwhile serious difficulties had appeared with the Bazooka. The basic theory of this weapon assumes that the burning of the charge is completed before the projectile leaves the muzzle of the projector. The double-base charge used in this weapon, however, burned beyond the muzzle of the projector when fired at a temperature of 70 F or less. This subjected the rocketeer to discomfort and even to serious injury from the expulsion of powder fragments near the end of burning, and increased the dispersion materially. Attempts to improve the situation by modifying the granulation led to the danger of blowups from the high pressures encountered under warm weather conditions. Gun-shy from the painful fragments and doubtful of the precision of their weapon, Bazooka operators were suffering severe casualties and were not getting the desired operational results. A shift from the double-base charge to an all EJA charge stopped the blowups and stopped beyond-the-muzzle

[f]This section is based on a summary supplied by Louis P. Hammett and J. F. Kincaid.

burning over a range of temperature much wider than encountered in operational use, but the smoke resulting from the potassium perchlorate revealed the position of the rocketeer and completely excluded the use of EJA powder for this or other ground-launched weapons.

After trials with various compositions it was found that a powder called BBP (Blastless Bazooka Powder) or T-4, containing only 7.6% of perchlorate, has a temperature coefficient only one-half that of the standard ballistite. With this powder, burning can be kept within the launcher down to 0 F, and the amount of smoke is small enough to be tolerated.[72] This powder was immediately adopted for Service use, and production started in April 1945. A new, heavier, and more effective Bazooka projectile was later designed around this powder and was, indeed, possible only because of it. This was upon the point of production when hostilities ceased.

EJA powder and similar materials containing large proportions of potassium perchlorate-carbon black filler again became the subject of active study early in 1945, since they are ideally suited for use as rate control strands in cast double-base charges (Section 6.5), and it then became evident that most of the production difficulties encountered a year earlier could be obviated by minor changes in composition.

Another powder, MJA, also extensively developed, contains potassium nitrate instead of the perchlorate of EJA. It is slower burning and has a lower specific impulse. It turned out to be ideally suited to the 115 mm rocket developed at the Allegany Ballistics Laboratory, yielding a projectile velocity of 1,200 fps, compared with 950 fps from a double-base charge, and having a performance essentially independent of temperature. Enough powder for extensive tests had been prepared by the Radford Development Department when hostilities ceased.[73] Whether the powder would have reached Service use depended upon whether the 115 mm rocket was finally adopted. This in turn depended upon a conflict between the Service desire for standardization on a single weapon, the HVAR which used large web dry-extruded powder, and the availability of large and unused facilities for the production of solvent-extruded powder, compared with limited and difficultly obtainable equipment for dry extrusion.

These powders are prepared by the methods and in the equipment employed for the preparation of solvent-extruded gun and rocket propellants. With the faster burning compositions such as EJA, existing plants are, however, not usable because safety prescribes heavier barricading and wider dispersal of equipment. The ingredients are mixed in a sigma arm mixer in the presence of a sufficient amount of volatile solvent (ether-alcohol, acetone, or mixtures) to form a dough. This is extruded through dies mounted in hydraulic presses, and the strands formed are dried at temperatures of the order of 130 F or less in a current of air for a time which depends upon the web thickness and composition of the powder. Adjustment of kind and amount of solvent, time and temperature of mixing, temperature and rate of extrusion, drying time and temperature must all be made for each particular composition if powder of adequate strength and freedom from flaws is to be attained.

The maximum diameter of solvent-extruded composite propellants which have been prepared by direct methods is approximately 1.5 in. Since the production of larger sizes was desirable, the possibility of dry extruding the solvent-extruded rods or granules was investigated. The project had passed the preliminary exploratory stages and serious investigation was contemplated at the end of the war. A promising composition of this type (EDX) is described in Table 2.

The experience in the attempt to transfer a small-scale laboratory process for the production of EJA powder almost directly to full-scale production equipment had made it painfully apparent that any group concerned with the development of new powders should have available, under its own direction, an experimental plant capable of making enough powder for extensive testing, and in which the results of tests could be immediately transferred to improved techniques of production. No such expansion was possible on the Bruceton grounds, but an agreement was made for the construction of an experimental plant at the Allegany Ballistics Laboratory, the central laboratory of Section H, NDRC Division 3. The technical staff and research direction of this plant were supplied by the Explosives Research Laboratory, nontechnical staff and administration by the Allegany Ballistics Laboratory. Construction started in June 1944, and the first batches of powder were made in December of the same year. The operations were highly successful; much of the development of the BBP and MJA powders was carried out in the Allegany Ballistics Laboratory, and it was possible to turn over to the Radford Development Department essentially complete directions for full-scale produc-

tion of these powders. In early 1945 the laboratory was easily expanded and converted to the development of the cast double-base charge, including the production of the rate control strands. In most respects this plant could serve as a model for an experimental developmental establishment for propellants. The whole operation was under a single technical control; the scale was small enough to permit the production of a large number and variety of experimental compositions and large enough to allow the preparation of sufficient powder of the largest granulations for reasonably extensive testing in full-scale charges for the weapons of interest; and the static and flight testing facilities of the Allegany Ballistics Laboratory made possible rapid testing and reporting of each new material.

Table 2. Composition and ballistic properties of solvent-extruded composite propellants.*

Designation	EJA	BBP	MJA	EDX†
$KClO_4$‡	56%	7.8%	....	....
KNO_3	....	....	43%	43%
Carbon black	9	1.2	7	7
Nitrocellulose (12.6%N)	21	....	....	23
Nitrocellulose (13.1%N)	....	54.6	26	....
Nitroglycerin	13	35.5	21.5	22
Ethyl centralite	1	0.9	2.5	5
I (impulse)	152 sec	168 sec	130 sec	150 sec
d (density)	2.02 g/cc	1.68 g/cc	1.8 g/cc	1.83 g/cc
Id	307	280	240	275
n (pressure exponent)	0.45	approx 0.7	0.46	0.54
R_{2000}	1.90 in./sec	....	0.70 in./sec	1.45 in./sec
Temp coef	0.003	0.010	....	0.003

*I, the specific impulse in seconds, is given for a chamber pressure of 2,000 psi and unit expansion ratio. The values for other expansion ratios may be estimated from OSRD-1627. Because of the greater heat losses with the small motor used, the specific impulses given in the table are substantially less than those that would be obtained in large motors. The small motors which were used give a value of 165 for I and of 270 for I_d for modified Bullseye powder.

†The formula for EDX includes 0.6% of added magnesium stearate, included to improve extrudability.

‡The $KClO_4$ contains 0.5% magnesium oxide and 0.5% magnesium tearate as anticaking agents.
s

6.4 CAST PERCHLORATE PROPELLANTS[g]

The Galcit propellants, mixtures of potassium perchlorate and asphalt developed at the California Institute of Technology, are outstanding for their ease of preparation and for the simplicity of the equipment in which they are prepared. Compared with many other propellants they have the additional major advantages of a low temperature coefficient of the linear burning rate. They have, however, when used at very high or very low temperatures, shown deficiencies which are probably unavoidable in materials of a pitchy or asphaltic nature. Such materials become soft enough to flow at high temperatures and become hard and brittle at low temperatures. Since it was known that the physical properties of long chain, high molecular weight polymers, and especially elastomers, change much less with temperature, an investigation was begun in the latter part of 1944 at the Explosives Research Laboratory looking toward the development of a castable propellant based on potassium perchlorate and a suitable high polymer.

It was clear from the start that the most desirable material would be one which was initially a liquid of moderate viscosity and which could be converted, after casting, to a rubbery polymer by chemical action at not too high a temperature. Materials with these properties are not common, particularly when the added qualifications are made that the initial liquid should not be highly volatile and that its polymerization should not be accompanied by large shrinkage. The earliest development made use of a thermoplastic mixture of ethylcellulose and castor oil. A 25/75 mixture of ethylcellulose-castor oil and potassium perchlorate showed some advantages over Galcit. This mixture was improved ballistically by the addition of 5% of aluminum flake. It was still, however, subject to too narrow useful temperature limits.

The next development was based on the General Electric Company's Permafil resins. These resins are sufficiently fluid originally to permit casting a suitable mixture with potassium perchlorate at room temperature. In the presence of a peroxide catalyst the mixture sets up overnight at 60 C to a gel of about the consistency of art gum. After polymerization the mixture does not flow at 140 F and is still rubberlike at —40 F. The recommended composition is

74.5% potassium perchlorate,
0.5% carbon black,
24.6% Permafil 2851,
0.33% t-butyl perbenzoate.

The process involves grinding the perchlorate to a controlled particle size; mixing the ingredients in a kettle or dough mixer, preferably under vacuum; casting in suitable metal molds; heating at 60 F for two days; removing the casting from the mold; and applying the restricting material to the casting.

The product obtained in this fashion has a specific impulse of 170 seconds at 1,000 psi and optimum expansion, a density of 1.81 g per cc, an exponent of 0.70 in the burning law, a burning rate of 0.72 in.

[g]This section is constructed from material furnished by Louis P. Hammett and Harley Hardman.[74,75]

per second at 1,000 psi and 70 F, and a restriction ratio of 182 under the same conditions. The temperature coefficient of pressure, thrust, and burning time at constant restriction ratio is 0.6% per degree centigrade.

This development was so promising that a pilot plant for further study of the preparation and properties of cast perchlorate propellant was designed and had been partly constructed by the time hostilities ceased. Further work remains to be done, particularly to secure neutral burning and to permit restriction of burning surfaces for low temperature firings, before the cast perchlorate propellant can be considered a completed development. There seems to be no reason to doubt, however, that this additional work can be carried through successfully.

6.5 CAST DOUBLE-BASE POWDER[h]

During the course of World War II it became apparent that there were needs for giant grains of rocket propellants for a number of important applications. These applications included towing of "Snakes" for mine clearance, assisted take-off of aircraft, and the launching and propulsion of guided missiles. By the fall of 1944, two types of rocket propellants, molded composite propellant and Galcit (see Sections 6.2 and 6.4), had been developed to fill these needs. While both these materials had many excellent characteristics, they had one defect in common: both produced large volumes of white smoke on firing. This made them unsuitable for many applications. Double-base powder, by contrast, is smokeless, but, unfortunately, no fabrication method existed which was suitable for the preparation of sufficiently large grains of double-base powder for these applications.

In the fall of 1944 work was begun at the Explosives Research Laboratory looking toward the development of a method of fabricating very large grains of double-base powder by exploiting the tendency of nitrocellulose strands or granules to swell and coalesce when immersed in a suitable solvent. It was hoped that a solvent which was sufficiently nonvolatile, sufficiently active, and which had adequate explosive potential could be devised by mixing a liquid explosive such as nitroglycerin with some reasonable proportion of a nonvolatile nonexplosive material. It seemed possible that when the slurry of finely granulated nitrocellulose-base propellant was mixed with the solvent the granules of casting powder would coalesce, due to the diffusion of liquid into the nitrocellulose and the resulting increase in the volume of the solid phase. In preliminary experiments to test this hypothesis, a mixture of 80 parts of nitroglycerin and 20 parts of diethyl phthalate was chosen as solvent for the initial test. A ball powder having a mean ball diameter of 0.020 in. was available. The initial castings were prepared by forming a slurry of the two ingredients, evacuating to remove air, and curing for two days at 60 C. Partial burning of the castings at 8,000 psi indicated that they were of excellent quality. The partially burned surfaces were perfectly smooth, aside from a faint surface pattern reminiscent of the original heterogeneous structure of the slurry. Because this preliminary experiment was so successful, serious attention was immediately given to the development problems involved.

In January of 1945, enough experimental data had been collected to make it reasonably clear that the process worked essentially as outlined above, and the industrial development of the process appeared to be a feasible undertaking. At that time a new principle for controlling the burning rate, temperature coefficient, and pressure exponent of double-base propellants was suggested by the California Institute of Technology. The proposal was that a number of strands of some material having good ballistic characteristics be imbedded in an end-burning charge of double-base powder in the form of long strands running parallel to the axis of the grain. It is necessary that these strands be faster burning under all operating conditions of temperature and pressure than the matrix which surrounds them and that they be tightly bonded to the matrix so that burning cannot proceed down the junction of the two materials. This method of controlling the ballistic characteristics of cast double-base propellants was particularly attractive since the material of choice for the rate control strands, solvent-extruded composite propellant was at hand as the result of an earlier development (see Section 6.3). Solvent-extruded composite propellants have excellent ballistics. They produce smoke on burning and they are difficult to prepare in large webs, but these two disadvantages were not of importance in their use as rate control strands, since the proportion required (1 to 2%) was too small for the smoke to be significant, and the rate control strands need not have large diameters.

The combination of the casting process for fabricating double-base powder with the rate control plan in-

[h]This section is constructed from information supplied by John F. Kincaid.[76-80]

troduced the possibility of preparing propellants combining all the advantageous properties of both straight double-base and solvent-extruded composite propellants. These included the good mechanical properties, smokelessness, and high impulse characteristic of double-base propellants, with the flexibility of burning rates and low temperature coefficients characteristic of the composite materials. The unique advantage to be gained by such a grain (later christened Type I castings) may be illustrated by discussing an old problem frequently encountered. In double-base powders and to some extent in composite propellants, there exists a correlation between the flame temperature and the burning rate of the materials. The faster burning materials, having high flame temperatures, are required for many applications. At the same time low flame temperatures are frequently desirable in order to eliminate flash and reduce nozzle erosion and motor heat-up. It can be seen that the rate control plan offered, for the first time, the possibility of independently controlled flame temperature and burning rate, since the burning rate can be varied by variations in the rate control strands which constitute too small a proportion of the entire charge to be thermochemically significant.

Until the proposal of the rate control principle, the research objectives of the group working on the cast double-base process had not been clearly defined, since attention was directed toward a general study of the significant features of the process. After this plan became available, however, it was clear that an end-burning charge could be constructed having a diameter of 8 to 9 in. and operating at a pressure of 1,500 psi or less, which would deliver a thrust of 1,000 lb. Such a charge would be smokeless, could be loaded into the currently available Aero Jet motors, and, since it was end burning, would completely fill the available motor space aside from the volume required for restriction and a reasonable clearance. This charge was considered to be an ideal answer to the Navy's need for an 8-second, 1,000-lb thrust, smokeless unit for the jet assisted take-off of aircraft from carriers, and the development of this charge was made the top objective of the group.

The status of this development program when NDRC work was terminated in November 1945 is outlined below.

6.5.1 Composition

The effect of variations in composition on the mechanism of consolidation has been extensively studied at the Explosives Research Laboratory and at Cornell University. The significant variables appear to be well understood. For example, it has been demonstrated that matrices of good quality can be obtained consistently. The effects of varying the composition of the casting powder and/or the composition of the solvent have been thoroughly studied, and it has been possible to find quick solutions for the development difficulties which have arisen from time to time. The composition of the casting powder, casting solvent, and rate control strands which are currently standard for this application are given below.

Casting Powder	Per Cent
Nitrocellulose (13.15% N)	74
Nitroglycerin	20
Diethyl phthalate	5
Centralite	1
Carbon black (added)	0.5

Casting Solvent	Per Cent
Nitroglycerin	65
Dimethyl phthalate	34
Centralite	1

Rate Control Strands	Per Cent
$KClO_4$	56
Carbon black	9
Nitrocellulose (12.6% N)	25
Casting solvent	9
Centralite	1

6.5.2 Fabrication Methods

Two fabrication methods are currently favored. One, thoroughly studied by the Division 8 group at the Allegany Ballistics Laboratory, is known as the *increment* method. In this method the grain is fabricated by successive additions of casting powder and solvent in increments to the container. A previous evacuation of the ingredients allows the formation of a product free of holes. The ingredients are mixed by carrying out the addition with the container mounted on a shaking machine of industrial design. The rate control strands are held in place by spiders at the top and at the bottom of the container and are mounted in place before the addition of the other components. Another method proposed and initially developed by a group working at the Kenvil Plant of the Hercules Powder Company is known as the *bottom-filling* method. In this method the evacuated casting powder and the rate control strands are placed in the container before any solvent is added. The evacuated solvent is then flowed into the container through a hole in the bottom under a gravity head. The bottom-filling

method has received somewhat less attention than the increment loading method, but experience with it has been highly favorable, and it is anticipated that this method will be an excellent industrial fabrication technique.

6.5.3 Restriction

After preliminary experiments it was decided that end-burning grains of the type desired could best be prepared by casting the components into a plastic container which would then serve as the restrictive coating without additional modifications. This method has proven to be highly successful and convenient. After an investigation of a large number of plastics, including Saran, a number of vinyl polymers, Bakelite, Beetle, cellulose acetate, cellulose acetate butyrate, Lucite, ethylcellulose, and polystyrene, the field was narrowed to cellulose acetate, ethylcellulose, and Lucite. Other materials either proved to be too inert to bond with the castings, e.g., Saran, or softened too readily under the influence of the nitroglycerin, e.g., cellulose acetate butyrate. Currently, cellulose acetate is regarded as the best material for restrictive containers. The containers actually used have been largely fabricated by a convolute wrapping method from 10-mil cellulose acetate sheets, but an injection molding method appears feasible and should be investigated.

6.5.4 Service Evaluation

Approximately 300 grains 8½ in. in diameter and weighing 40 to 75 lb have been prepared. Evaluation of the experience gained with these grains and with some 1,400 subcaliber units 4 in. in diameter leads to the following conclusions.

Grains which have satisfactory ballistic characteristics at room temperature and elevated temperatures can be consistently prepared. There remain some difficulties with low-temperature firing behavior and with cycling, but it appears probable that additional development will solve these difficulties. The high-temperature aging characteristics of the centralite-stabilized composition given above are not so good as would be desirable, and considerable effort has gone into the study of this characteristic. Failure on storage at high temperatures is caused by the formation of gas within the grain. Gas formation is a normal phenomenon for double-base powders, but difficulty with it had not appeared until rather large grains were fabricated. This is due to the ease with which the gaseous decomposition products can diffuse through thin web materials. It has been observed that the substitution of carbazole for centralite as a stabilizer causes an enormous increase in the high-temperature storage life. While carbazole-stabilized materials are unsatisfactory, due to difficulty with consolidation, a new stabilizer, 2-nitrodiphenylamine, has been discovered which, it is hoped, will have the advantageous characteristics of both centralite and carbazole. The possibility that the normal exothermal decomposition reaction of such large grains would cause self-heating and eventual spontaneous explosion has been carefully studied, and it has been found that no difficulty from this can be expected with solid grains 8½ in. in diameter. It is probable that very much larger grains can also be safely prepared.

It seems probable that cast double-base propellants are a nearly ideal material for the fabrication of very large grains for thrust applications. Type I grains, those having axially dispersal rate control strands, appear to be particularly suitable for thrust units having burning times of 8 seconds or more, and thrusts of 500 to 2,000 lb. Double-base castings without rate control powder (Type O), or castings containing rate control powder in the form of uniformly dispersed granules rather than long strands (Type II), can be used for the fabrication of single or multiperforated grains having short burning times and high thrusts. Since such short-burning, high-thrust units appear to be badly needed for the launching of guided missiles, additional development work on Type O and Type II castings is very much in order. Development of these materials has thus far been of a preliminary character only, since so much emphasis was placed on the development of the Type I castings.

A number of specific recommendations for future work are possible in the light of this experience. The more important of these follow.

1. Type O and Type II castings should be carefully investigated.
2. The consolidation and ballistic characteristics of castings prepared from casting powder containing low nitrogen (12.6 or 12.2% N) rather than high nitrogen (13.15% N) stock should be investigated with the expectation that the consolidation characteristics of such casting powder will be much better than those of the standard powder now in use. This would allow the preparation of many compositions which would not consolidate well if nitrocellulose of high nitrogen content were used in the casting powder.
3. 2-Nitrodiphenylamine, and, possibly, other stabilizers, require careful and large-scale evaluation, in view of the observation at the Explosives Research

Laboratory that the rate of gas production from double-base powder varies enormously with the stabilizer.

4. Additional study of the fabrication of containers and of their storage life at normal ambient temperatures needs to be carried out. An injection molding method of fabrication is particularly recommended.

6.6 NOZZLE DESIGN AND MATERIALS[i]

The work of the Explosives Research Laboratory on the development of new jet propellants, described in Sections 6.2 to 6.5, required the construction of motors for static firing tests. As interest in jet propellants turned to large long-burning charges, the problem of erosion of the motor nozzles became acute. Large numbers of charges had to be tested, and the fabrication of nozzles was both expensive and a serious burden on machine-shop facilities. Further, no adequate conclusions could be drawn about the behavior of a single propellent charge unless the throat area of the nozzle remained essentially constant during the burning. For these reasons the requirements for test motors are more severe than for Service motors, and it was necessary to study, as a problem in itself, the design and construction of nozzles.

The conclusions from this study[81,82] are consistent with the idea that a nozzle erodes or does not erode depending on whether the temperature of the surface layer exceeds or does not exceed the melting point of the nozzle material. There is no evidence to suggest that specific chemical attack is involved or that the high-temperature strength of the material is of importance. The same conclusions have appeared from work on gun erosion. More specifically the results are:

1. The flame temperature of the propellant is a major factor. Because the necessary thermodynamic data for the accurate calculation of the temperature of propellants containing large quantities of alkali salts are lacking, this conclusion is qualitative rather than quantitative; but the difference in erosion between composite propellants containing 10 to 15% of alkali nitrate and those containing around 50% of alkali nitrate are very large and unmistakable. The more erosive compositions with higher nitrate content undoubtedly have higher flame temperatures.

2. Erosion increases markedly with increasing chamber pressure. The effect is large and of great practical importance.

[i]This section is constructed from a summary prepared by L. Axelrod.

3. Erosion is greatest at the throat and in the nearby regions upstream in the gas flow. If this region can be protected against erosion, no other need give concern except when grid supports or other obstacles directly interfere with the gas flow.

4. The melting point of the nozzle material is of prime importance. Molybdenum, which may take the form of a relatively small insert in the critical throat area, has been most serviceable. Pure chromium and tungsten carbide have also performed well in limited tests. Heat capacity and conductivity are also important, since high values lower the surface temperature; copper is consequently more resistant than steel. For the same reason the mass of the nozzle is a factor of importance, and a large, heavy nozzle is more resistant than a small, light one. Alloys, which have lower conductivity and usually lower melting points, are less resistant than pure metals.

5. Given the same propellant and the same burning time, erosion is more severe with small charges than with large charges because the former require the use of small nozzles. This conclusion is definite and based on comparative tests with two different propellants. The effect probably arises from the fact that nozzle mass and heat capacity vary as the cube of the linear dimension, heat transfer as the square.

6. The geometry of nozzle and of nozzle entrance area are of overwhelming importance. Designs based on qualitative considerations of reducing turbulence in the gas flow have led to a great decrease in erosion. Unfortunately no quantitative theory is available but Figure 2 illustrates the points which have been found empirically to be significant.

a. The gas former region should be the frustum of a cone extending to the full diameter of the motor. A 45° angle is satisfactory. Reverse curvatures (S-shaped configurations) have not performed well, probably due to the fact that a small radius of curvature becomes necessary in the entrance if the curvatures in the gas former, entrance, and throat are to blend well into one another.

b. The gas former should be tangent to the curvature of the entrance of the nozzle. The radius of curvature ρ of the entrance should be as large as possible.

c. This curvature should carry through the throat and blend smoothly into the expansion cone. There should be no straight portion at the throat. Nozzles designed according to this scheme have the same radius ρ, about a center F, from the 45°

cone through the throat and to the 30° expansion cone.

d. All irregularities should be avoided and finish should be smooth, though a high polish has not appeared to be necessary.

e. The wall thickness of the nozzle and hence its total mass can be adjusted by cut and try procedures to the propellant and burning time concerned.

f. The expansion angle has little effect on the efficiency of the nozzle, provided the angle is between 20° and 40°.

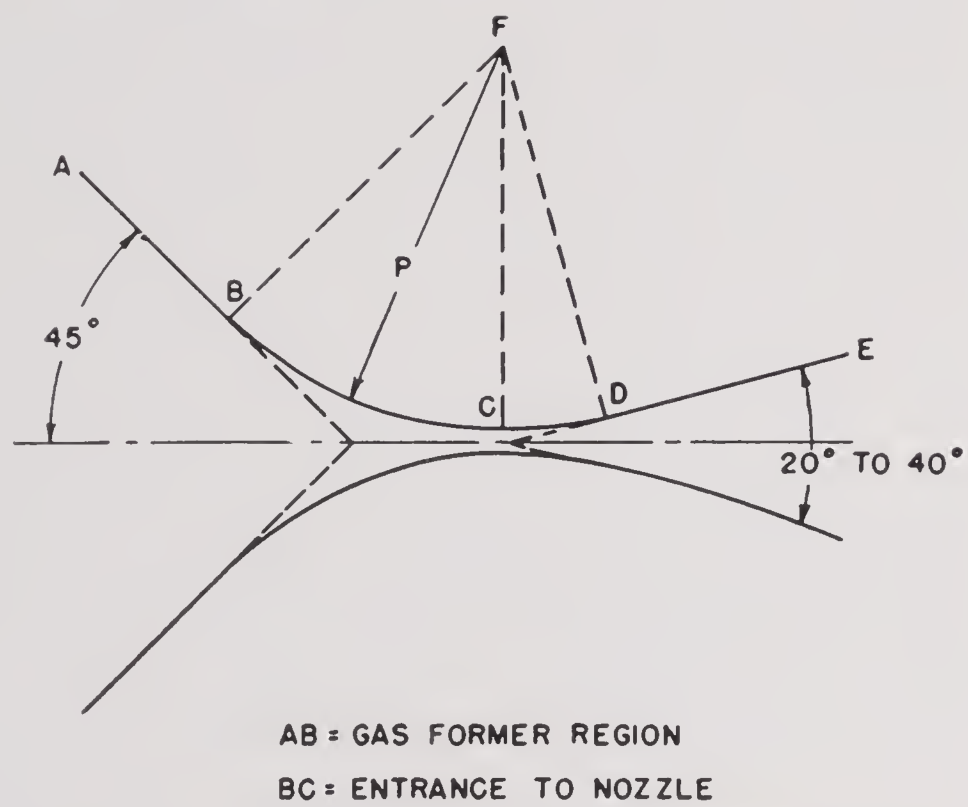

FIGURE 2. Geometry of nozzle and nozzle entrance area.

With nozzles designed in this way of steel or, for more severe conditions, of copper, satisfactory performance for single shots has been attained with all of the charges of interest to this laboratory. Most nozzles will also withstand numerous repeated shots.

Some special observations have been made on particular materials. Steel nozzles of proper design to withstand repeated firings usually fail by the appearance of checks on the throat. These checks enlarge to cracks in which extensive erosion then takes place. Under the same condition copper fails, if it fails at all, by actual melting. Comparative tests under highly erosive conditions showed that the resistance of iron alloys decreased in the order SS501, SAE 2515, SS440, SS4321, and Armco iron. Tests on steel and copper nozzles coated with tungsten, molybdenum, or chromium showed little if any advantage gained by the coating. In one nozzle a thin sheet of tantalum was rolled inside a steel nozzle to conform to its contours. This survived several shots, after which blisters formed and eroded. The chief difficulty with all types of coatings is to obtain sufficient adherence to the base metal. Most coatings tear off during the tests.

Graphites investigated in the form of large inserts supported in steel were the C-18, AGX, A12, and AMF grades of the National Carbon Company. They had densities varying from 1.52 to 1.69. The lower density grades tend to erode, the higher density ones to crack. Usable nozzles for some applications have been made, but well-designed metal nozzles are probably more reliable.

Many ceramic materials have been tried as inserts. All eroded and many cracked from thermal shock. In view of their light weight and economy in mass production they may well deserve further study, particularly in the direction of using very high-melting oxides bonded with a minimum amount of fluxing agent.

6.7 ALBANITE POWDERS[j]

At the outset of World War II, an urgently needed improvement in gun performance was the elimination of secondary flash from 6-in. to 8-in. caliber cannon. The current propellant of least flashing tendency, namely FNH with incorporated potassium sulfate, did a passable job in guns up to 5 in., but it was objectionably smoky and it flashed in all the larger weapons. Early in 1942, the problem rose dramatically in importance with the advent of nighttime naval engagements, when the blaze of flight from the ship's own guns so blinded its personnel as to interfere with fire control.

In Project NO-135, the Navy asked Division 8 to develop flashless propellants for pertinent existing guns. Work was begun at the Explosives Research Laboratory, and, beginning in May 1943, promising formulas were carried into the semi-works phase under Contract OEMsr-763 with the du Pont Company; this study led to the first proof firing of Albanite in March 1944.[k]

Preparation of pilot scale quantities of Albanite extended from July 1944 to November 30, 1945, under Contract OEMsr-1355, also with the du Pont Com-

[j] This section is constructed from a report written by H. H. Holmes.

[k] For details of the work done at the Explosives Research Laboratory, see reference 83; for details of the work done at the Burnside Laboratory of the Explosives Division of E. I. du Pont de Nemours & Company, see reference 84. Small-scale studies of the preparation and properties of *solventless* powders containing DINA and other materials in place of nitroglycerin are reported from the California Institute of Technology[85] and are discussed in Section 6.10.

pany. The success of the powder in medium-sized guns prompted its trial in cannon as large as 16 in. and in smaller weapons down to 40 mm, the latter with the hope of obtaining ammunition which is at the same time smokeless and flashless.

The only promising solution of the problem lay in a propellant having a flame temperature lower than that of Pyro or FNH. The low heat evolution and high gas volume of nitroguanidine strongly recommended its use; indeed, nitroguanidine had been tested several times during the last fifty years and had been rejected principally for lack of a ready supply in this country. By 1942 Canada was making nitroguanidine in commercial quantities, and the British were using in some of their guns the following composition, called Cordite N.

Nitrocellulose (13.1% N)	19.0 parts
Nitroglycerin	18.5 "
Nitroguanidine	54.7 "
Ethyl centralite	7.5 "
Cryolite (K_3AlF_6)	0.3 "
Chalk	0.15 "

Cordite N is about equal in force to Pyro and NH, and its estimated flame temperature is 2430 K, as compared with 2580 K for the two American powders. Two disadvantages discouraged its adoption by the United States: (1) the health and explosion hazards of nitroglycerin volatilization and (2) the low mechanical strength of the composition in multiperforated grain form, especially at low temperatures. Samples of Cordite N, with 1.5% K_2SO_4 added, were made at the Nobel Works of Defense Industries, Limited, for the Navy 6-in./47 gun; in tests at the Naval Proving Ground, the powder gave essential flash suppression under severe conditions and was superior to the best single-base combination, FNH + 4% K_2SO_4. Cordite N later was proved flashless in major caliber cannon, and the Navy procured several million pounds from Canada as a temporary expedient; the fleet, however, never used it in regular operations, so that the experiments served principally to clear the way for a nitroguanidine formula containing a less volatile substitute for nitroglycerin and having good physical properties.

The physical incompatibility of nitroguanidine with nitrocellulose demands a high proportion of plasticizer in order to secure workability and strength in the finished colloid. It follows that most of the plasticizer content must have explosive potential. A paper survey of the explosives field eliminated most compounds on one or more of the following counts: volatility, lack of plasticizing action, chemical instability, sensitiveness to detonation, hygroscopicity, unavailability. The remaining candidates then were prepared and incorporated into a propellant formula similar to Cordite N. The candidates were:

Common Name	Chemical Name
Emmett	Ethyltrimethylolmethane trinitrate
GGTN	Glycerol monoglycolate trinitrate
GLTN	Glycerol monolactate trinitrate
DINA	*Bis*-nitroxyethyl nitramine
Fivonite	Tetramethylolcyclopentanone tetranitrate
Sixonite	Tetramethylolcyclohexanone tetranitrate

Emmett was rejected for lack of solubility in nitrocellulose and because it was about half as volatile as nitroglycerin. GGTN was dangerously unstable in the free state and in propellent mixtures. GLTN was unattractive because of difficulty in preparing the monolactate free from unesterified glycerol. Sixonite proved generally similar to Fivonite but had a lower potential with no compensating advantages. Of the two remaining explosives, DINA exhibited fair plasticizing action and was only one-tenth as volatile as nitroglycerin, and Fivonite was still less volatile, but compared with DINA it was relatively low in potential and was a poor plasticizer. In view of the current emphasis on low volatility and the urge for speed in development, DINA emerged as the most expedient material.

Propellant manufacturing techniques and ingredients then were studied on a 10-lb batch scale with a 4-in. diameter extrusion press, pointing for a medium-caliber powder which could be made in the plentiful American solvent-type equipment. Pyro nitrocellulose (12.6% N, 8- to 20-second viscosity at 10% in acetone-alcohol) produced the toughest and most workable colloid out of a list including 13.15% N blends of 13.4 and 12.6, with high, normal, and low viscosity; 13.0% N direct-nitrated; 12.0% N direct-nitrated. Various combinations of acetone, ethyl ether, and ethyl alcohol were tried as volatile solvents, and acetone-alcohol from 1/1 to 2/1 was chosen on the basis of workability and ingredient dispersion. Mechanical grain strength was markedly improved by replacing part of the centralite with a more active nonexplosive plasticizer, e.g., dibutyl adipate, dibutyl phthalate, triacetin, or DNT oil. (Other effective, but less attractive, adjuvants were Nylon, Neoprene, or ethylcellulose. Surface active agents such as soya lecithin or stearylamine were only slightly effective.) The manufacturing process comprised mixing at 45 C with 13 parts acetone-alcohol per 100 parts powder formula, blocking, extruding in multiperforated form, cutting to the same grain length

as corresponding NH powders and drying in air at 50 C for 5 days more or less, depending on web size. Out of this research came the Albanite formula.

Nitrocellulose (12.6% N)	20.0 parts
DINA	19.5 "
Nitroguanidine	55.0 "
Dibutyl phthalate	4.0 "
Ethyl centralite	1.5 "
	100.0 "
K_2SO_4 to suit pertinent weapon (1.5 parts K_2SO_4 for 6-in./47 gun)	0 to 5 parts
Volatile solvent (approx)	0.2 "
Moisture, less than	0.1 "
Adiabatic flame temp (1.5% K_2SO_4)	2390 K
Potential ($C_v T_0$, cal/g)	870
Force relative to Pyro powder	98%
Burning rate relative to Pyro (approx)	75%

A sample of Albanite, meeting standard ballistic specifications, was fired in the 6-in./47 in comparison with (1) an analogous sample made with Fivonite, (2) Cordite N + 1.5% K_2SO_4, (3) Pyro + 4% K_2SO_4 and (4) regular Pyro. Albanite and its Fivonite analog were essentially flashless under the most severe conditions. They were marginally superior to Cordite N, and all the nitroguanidine powders were far superior to the Pyro samples which gave blinding flashes of greater or less intensity.

Albanite has these further advantages over Pyro and NH: low hygroscopicity (0.3% moisture at equilibrium in 90% relative humidity at 30 C), and low residual solvent content, both making for ballistic stability; and a reasonable expectation of lower gun erosion rate. NDRC, Division 1, tests at the Franklin Institute place Cordite N and Albanite among the least erosive of current propellants.[86] Navy gun firings have demonstrated double gun life for Cordite N versus Pyro, and performance at least as good is expected for Albanite. Its chemical stability appears assured in that samples have withstood storage at 65.5 C for more than two years without a failure.[36,37,70] Its grain strength, according to side impact test, is only about 70% of Pyro or NH at −20 C, but is 170% of Cordite N at the same temperature.

Phase equilibrium studies at Cornell University[87] showed that DINA is soluble in Pyro nitrocellulose to the extent of only a 23/77 ratio at 26 C. The rate of crystallization of DINA from a 50/50 supersaturated colloid, however, is very slow. Microscopic examination of finished Albanite grains revealed some 5% of the DINA crystallized on or near the surface, but the proportion of crystals did not increase appreciably during several months' storage, and no significant internal crystallization was detected. A storage program coupled with closed chamber burning rate tests revealed no change in ballistic properties during 9 months' storage at the following temperatures: −40 C; + 40 C; cycling between −40 C and + 40 C; atmospheric temperature. Special tests proved that substantially no DINA dust can be removed from the grain by tumbling. The crystallization of DINA, therefore, is not regarded as an important quality factor.

An analytical procedure for estimation of the proportions of the ingredients in Albanite was developed.[88] Toluene is used to extract DINA, centralite, and dibutyl phthalate. DINA is determined by volumetric reduction with ferrous ion, centralite by volumetric bromination, and dibutyl phthalate by difference. Nitrocellulose is weighed as such after water extraction, and potassium sulfate is determined by a conventional method in the water solution. Nitroguanidine is estimated by difference.

Although the solvent-wet colloid and finished Albanite are insensitive to detonation by 100 grams of 60% straight dynamite, dry nitroguanidine and its mixtures with nitrocellulose are cap sensitive. Further, the wet colloid contains so little solvent that its burning rate in mixers and presses is several times higher than single-base colloid, approaching that of 40% double-base solvent-type powder. It was unsafe, therefore, to make large trial lots in existing single-base factories where the operators are directly exposed to the equipment. Since suitable American capacity was not available in the summer of 1944, it was arranged to make three lots[89] at the Winnipeg Works of Defense Industries Laboratory, using DINA and Pyro (wood pulp) nitrocellulose made at de Salaberry Works:

46,400 lb for 6-in./47 (1.5% K_2SO_4)
lot VC-66-EX
3,000 lb for 8-in./55 (5% K_2SO_4)
lot VC-97-EX
15,000 lb for 16-in./45 (5% K_2SO_4)
lot VC-96-EX.

Manufacture was carried out in the machines regularly used at Winnipeg for Cordite N. Crystalline DINA was dissolved in acetone, and the solution added to the other ingredients in a kneader holding about 430 lb of powder formula. The mixed colloid was hand-tamped directly into 8-in. vertical extrusion presses. There was no macerating, blocking, or macaroni pressing equipment. Considerable experimentation and extension of mixing time were required to arrive

at a treatment which would completely disperse the nitrocellulose without the use of excessive quantities of volatile solvent. Especially in the 8-in. and 16-in. granulations, porosity in the form of solvent-air bubbles resulted in variable burning rates from batch to batch, and it was indicated that blocking and macaroni pressing might be required in eventual full-scale manufacture. Although careful bomb firings of batches and subsequent blending resulted in acceptable lot quickness, the finished grains were objectionably porous.

In proof firings in the respective guns, all three lots were flashless. Smoke density was greater than with standard flashing powders, as expected, but was judged acceptable by modern battle standards. Lots VC-97-EX and VC-96-EX performed within the velocity and pressure specifications, and gave satisfactory velocity uniformity. Although lot VC-66-EX (6-in./47) displayed poor uniformity when initially fired, later trials, in which the *previous round* effect was eliminated, resulted in generally satisfactory uniformity and acceptable velocity and pressure levels.

At the conclusion of these tests in the spring of 1945, a practical solution of the problem appeared within reach, processing difficulties notwithstanding. In the interest of speeding the development, the composition for the time being was regarded as fixed, and the final steps—process improvement, preparing additional proof lots for large guns, and arranging full-scale manufacturing facilities—were started almost simultaneously.

An OSRD pilot plant had been under construction at Burnside Laboratory since September 1944. It was designed for the safe investigation of hazardous propellent mixtures in full-sized machinery, and to this end the mixers and presses were surrounded with 10-in. reinforced concrete walls, covered with a light roof and remotely controlled. The principal equipment items were a solvent mixing tank, two 50-gallon Werner-Pfleiderer mixers, one macerator, one 11¾-in. blocking press, one 12-in. vertical extrusion press (also used for macaroni pressing), two cutting machines, and an air-drying house. Operation began on Albanite in February 1945. Between that date and November 1945, in the course of process studies some 200,000 lb of Albanite were made at Navy request.[90]

In view of the fact that DINA, either crystalline or molten, is almost as sensitive as nitroglycerin, it was desensitized at the Eastern Laboratory nitrating plant by mixing 90 parts molten DINA with 10 parts dibutyl phthalate.[91] The mixture, termed DDP, was received at the Albanite plant as a relatively insensitive frozen mass in metal pails of 50 lb net weight. The DDP was then melted by surrounding the pails with water at 70 C, and was poured into a solvent mixing tank, which already contained the acetone and additional dibutyl phthalate called for by the powder formula. The resulting "solvent mix" was ready for addition to alcohol-wet nitrocellulose, nitroguanidine, and potassium sulfate in the powder mixer.

A mixing treatment of about 2 hours at 45 C jacket temperature, with 300 lb net powder per charge, was required to disperse the nitrocellulose. The colloid was then cooled and stiffened by evaporating part of the volatile solvent in the macerator, after which it was blocked at 1,000 psi. Efforts to extrude the powder at this stage resulted in a highly porous grain. Greatly improved consolidation was obtained by macaroni pressing and reblocking prior to extrusion, and nearly all lots submitted for gun trials were made in this way. Even so, a variable degree of porosity persisted, particularly in the larger granulations, with the result that succeeding batches made under apparently identical conditions varied as much as 15% in quickness. This factor probably accounts for the failure of several lots to meet ballistic specifications and must be remedied in future research.

Basic lead carbonate was incorporated in some of the more recent granulations as an experimental decoppering agent, with the hope of replacing the conventional lead foil.

Four press explosions occurred in the pilot plant, all of which were believed due to compression of acetone-air pockets. One was violent enough to blow out the extrusion die and remove the building roof, but in no case was the press cylinder ruptured. The barricades served to prevent personal injuries.

In July 1945, the Navy requested facilities for Albanite manufacture at a rate of 4,000,000 lb per month. On the basis of equipment capacities determined at the DINA and Albanite pilot plants, plans were laid to make DINA at Holston Ordnance Works and the propellant at Indiana Ordnance Works. The end of the war interrupted the program at the design stage.

It has so far been demonstrated that nitroguanidine propellants are thermally and ballistically sound where flash and erosion are important considerations. Time now being available for more extensive research, the Albanite formula should be reviewed with emphasis on reproducibility of burning rate. The nitroguanidine used up to date is now known to be relatively coarse by modern British standards, and a smaller crystal

size may improve consolidation of the colloid. A plasticizer better than the DINA-dibutyl phthalate combination may exist;[92] butyl NENA and certain related explosives are known to be more soluble in nitrocellulose than is DINA, and diethylene glycol dinitrate deserves evaluation. Surface active agents might be of considerable help. Less promising are changes in type of nitrocellulose or volatile solvent. It is intended to carry on the work under Navy auspices.

6.8 RDX POWDERS[1]

The problem of improved gun propellants was up for discussion soon after the formation of the National Defense Research Committee. Both military and commercial propellants in this country had for decades used nitrocellulose or nitrocellulose-nitroglycerin mixtures as their principal explosive ingredients. It seemed probable that other materials with explosive potential could be used to advantage, and the investigation of new gun propellants was, therefore, made a part of the work of the Explosives Research Laboratory.[93] Since Burnside Laboratory, as the smokeless powder research laboratory of the du Pont Company, had equipment for and experience in this kind of work, a contract was negotiated to cover the study of propellants containing crystalline high explosives.[94]

While existing facilities were being modified so that experimental batches could be made safely on a 10-lb scale, the Explosives Research Laboratory examined a variety of propellent compositions on a 1-lb scale. The immediate goal of the investigation was to develop propellants capable of giving higher velocities than existing powders without exceeding permissible gun pressures and having as favorable flash, smoke, and erosion characteristics as possible. Calculations were made both at the Explosives Research Laboratory and at Burnside Laboratory for the selection of ingredients which could be used to this end. The calculations at Burnside were based on Hirschfelder's thermochemical work carried out for NDRC Division 1.[95]

The computations indicated that a combination of a high explosive with a strong deterrent would result in a powder of high potential with a relatively low adiabatic flame temperature. The latter is conducive to low gun erosion and reduced tendency toward muzzle flash. An investigation of explosives including TNT, PETN, DINA, RDX, tetryl, picrates, nitroguanidine, nitrocellulose, and numerous less familiar explosives, revealed RDX to possess the greatest thermochemical advantage. From a long list of deterrents, butyl stearate was selected as the most promising.

A propellent composition for cannon was then formulated, using RDX and butyl stearate with nitrocellulose as a binder to permit granulating. It was this type of composition which was investigated for ballistic, physical, and chemical properties.

It was obvious from the variety of ballistic problems involved that a single composition could not satisfy all the requirements in existing guns. A high-velocity cannon powder could not be flashless nor would it be suitable for rifles. Accordingly, adjustments had to be made in the composition to conform with the properties desired. The proportion of deterrent had to be lowered substantially in order to obtain sufficient potential for rifle powder. This permitted such small quantities of butyl stearate in the composition that dibutyl tartrate or triacetin was substituted in rifle compositions to assure adequate plasticization. Five compositions received particular attention: CC1, a flashless cannon powder with normal ballistics and reduced erosion; CC2, a high-velocity cannon powder with normal flash and erosion; CR1, a flashless rifle powder with reduced smoke, normal ballistics, and reduced erosion; CR2, a high-velocity rifle powder with normal erosion; CR3, a super-velocity rifle powder with increased erosion. The basic formula of each is given in the following tabulation:

	CC1	CC2	CR1	CR2	CR3
Nitrocellulose (12.6% N)	37.5	36.5	47.0	50.0	36.5
RDX	50.0	53.0	47.5	45.0	60.0
Diphenylamine	0.5	0.5	0.5	0.5	0.5
Butyl stearate	12.0	10.0	5.5	...	...
Dibutyl tartrate	...	...	...	4.5	...
Triacetin	...	...	...	...	3.0
K_2SO_4 (added)	...	...	...	0.7	0.7

The rifle powders were ordinarily coated with dinitrotoluene in varying amounts in accordance with the ballistics desired.

Granulations were prepared for trial in a number of guns, including .50 caliber, .60 caliber, 20 mm T31, 40 mm Army, 40 mm Navy, 75 mm Model 1897, 76 mm M1, 3-in. M5, Navy 3-in./50, 90 mm M1, and Navy 5-in./38. The results of early trials were encouraging.[86] For example, it was possible with the CC2 composition to increase the muzzle velocity of medium-caliber cannon about 100 fps with no increase in maximum gun pressure beyond that obtained with the current single-base Service propellants. On the strength of these observations, considerable effort was put forth to adapt the manufacturing process to avail-

[1]This section is based on information supplied by W. F. Jackson.

able single-base powder facilities. The du Pont Military Explosives Division, with the cooperation of Eastern Laboratory, engineered the production of a 30,000-lb batch of RDX of suitable fineness, desensitized with butyl stearate. The Division 8 propellant pilot plant at Burnside Laboratory studied the powder granulating process in full-scale equipment.

Manufacturing details were satisfactorily worked out, and the propellants were found to be acceptable with respect to erosion, flash, and smoke characteristics, mechanical grain strength, explosive sensitivity to shock, hygroscopicity, chemical stability, and volatility,[96] but they suffered from one serious defect: the ballistic uniformity was poor. Velocity variations in nearly all weapons were far in excess of those observed with the conventional M1, M2, or M6 compositions. In rifles, indications were that the uniformity could be made acceptable by adding extra igniter. This would probably require redesigning the case in many instances to accommodate a larger primer. In cannon, increased ignition was tried without success. It is probable that lack of ballistic uniformity in cannon is a result of the inherent progressive burning character of these compositions. An unusual sensitivity of burning rate to changes of pressure at a few thousand psi was observed in closed-vessel tests of the RDX powders.

Further work with RDX as a powder ingredient would call for fairly drastic revisions in the formulation. The ballistic advantages which would follow a satisfactory solution to the uniformity problem would repay considerable effort.

6.9 STUDIES OF NITROCELLULOSE[m]

Under the sponsorship of Division 8 a number of investigations of nitrocellulose were undertaken. The two earliest were nonexperimental surveys on the use of wood cellulose nitrates for munitions,[97] and on the conversion of nitrocellulose to smokeless powder.[98] Another group of studies dealt with the mechanism of gelatinization and solution of nitrocellulose.[99-101] Still another group of studies was made at the California Institute of Technology.[102,103] These studies will be considered under six separate headings.

6.9.1 Preparation of Samples of Nitrocellulose

In connection with studies of the nitrocellulose in smokeless powder, it is frequently necessary to extract the other constituents, and to free the residue from moisture and extracting solvent. The procedures currently employed for such separations are discussed in Section 6.11.1 in connection with the determination of nitrocellulose in smokeless powder. Unfortunately it was found that, although these procedures are satisfactory for the determination of the percentage of nitrocellulose in smokeless powder, they frequently caused significant alterations in some of the properties of the nitrocellulose.

Although no thoroughly satisfactory procedure has been developed for obtaining the nitrocellulose from a smokeless powder in a form suitable for further study, it has been found that uncolloided water-wet nitrocellulose can be dried either by vacuum desiccation at room temperature, or by heating at 70 C. Experiments at the California Institute of Technology indicated that dry nitrocellulose could be heated at 70 C for as long as 100 hours without any detectable change in its properties, but that slow degradation occurred during the same period at 100 C.[104]

6.9.2 Fractionation of Nitrocellulose

In connection with studies of smokeless powder of unknown composition, it was often desirable to determine the properties of the component nitrocelluloses which composed the blend used in the preparation of the powder. Therefore studies were made of procedures for the fractionation of nitrocellulose blends prepared from components having distinctly different percentages of nitrogen; no serious attempt was made in these experiments to extend these studies to the fractionation of unblended nitrocelluloses.

Several nitrocelluloses prepared by blending known amounts of materials containing 12.6 and 13.4% of nitrogen were fractionated into what appeared to be their original components by partial solution in 2/1 ether-alcohol at 25 C.[105] The same procedure was used to study the properties of the component nitrocelluloses in several captured German propellants,[106] but it was found that the nitrocelluloses in Japanese propellants could be fractionated more satisfactorily with the use of methanol.[107]

6.9.3 Chemical Characterization of Nitrocellulose

The chief method employed for the chemical characterization of nitrocellulose is the determination of nitrogen; procedures for this determination are discussed in Section 6.11.1.

Several observations have led to the conclusion that

[m] This section is based on a summary written by Richard M. Noyes of the studies made at the California Institute of Technology.

nitrocellulose may not always be sufficiently characterized by nitrogen content and viscosity alone. Some attempts were consequently made to establish the presence of groups other than nitrate and hydroxyl. Preliminary experiments failed to indicate detectable amounts of aldehyde groups in the nitrocelluloses investigated, and lack of time prevented further studies along this line.

6.9.4 Investigations of Molecular Weight and Molecular Weight Distribution in Nitrocellulose

Several procedures are available for determining the average molecular weights of linear polymers like nitrocellulose. Of these procedures, measurements of osmotic pressure, of viscosity, and of light scattering were selected as the most promising, and studies of these techniques were made.

1. *Measurements of osmotic pressure.* Procedures were developed for determining the number-average molecular weights of nitrocelluloses by means of measurements of osmotic pressure. These procedures appear to be quite satisfactory for the study of nitrocelluloses in double-base powders.

2. *Measurements of viscosity.* Viscosimetric procedures are those most frequently employed for studies of the molecular weight of nitrocellulose. Most commercial procedures involve only the purely empirical correlation of the properties of nitrocelluloses in terms of the viscosities of concentrated solutions prepared from them. Since the results of measurements on these concentrated solutions cannot be used to calculate the molecular weights of the solute nitrocelluloses, most of the studies at the California Institute of Technology were made on dilute solutions of nitrocellulose. A few studies of concentrated solutions were also made in order to facilitate the comparison of measurements on dilute solutions with measurements by standard commercial procedures.

The viscosities of dilute solutions of nitrocellulose in butyl acetate and in acetone were measured with capillary viscometers, and the results of these measurements were used to calculate weight-average molecular weights. Since molecular weights obtained by this procedure are only relative, it was necessary to obtain an absolute calibration by means of measurements on samples of known molecular weight. This calibration was effected by means of osmometric and viscosimetric measurements on carefully fractionated samples[108] which were believed to be molecularly homogeneous.

Measurements of viscosity on commercial nitrocelluloses are customarily made by means of a falling-ball viscometer on 10% solutions in 10/90 alcohol-acetone;[109] the results of these measurements are reported in Hercules seconds. This procedure requires a 20-g sample of nitrocellulose, and the precision claimed is only ± 3.8 per cent.[110] A modified capillary-type viscometer by means of which measurements can be made with the use of only one gram of nitrocellulose was developed at the California Institute of Technology.[111] This viscometer is satisfactorily precise for the measurement of viscosities of concentrated solutions, and the results can be converted to Hercules seconds by the use of a factor.

An attempt was made to extend to higher concentrations the results of viscosity measurements on dilute solutions of nitrocellulose in butyl acetate. These studies were discontinued because the viscosities of the concentrated solutions were found to be extremely sensitive to traces of moisture. The viscosity of a 5.50% solution of nitrocellulose in anhydrous butyl acetate is six times the viscosity of a solution of the same concentration prepared with butyl acetate saturated with water at 25 C.[112] This and other observations indicated the necessity for great care in the use of pure solvents in viscosity studies.

Viscosities of several nitrocelluloses were measured both in dilute solutions in butyl acetate, and in concentrated solutions in alcohol-acetone, and the results were used to prepare a graph for estimating the viscosity of a nitrocellulose in Hercules seconds from the result of a viscosity measurement on a dilute solution in butyl acetate.

3. *Measurements of light scattering.* Apparatus was developed at the California Institute of Technology for determining the molecular weights of nitrocelluloses by means of measurements of the light scattered at 90 degrees from the incident beam. The procedure usually gave results of the right order of magnitude, but more developmental work is needed before light scattering can be considered a reliable tool for measuring the molecular weight of nitrocellulose.

4. *Studies of the molecular heterogeneity of nitrocellulose.* The molecular heterogeneities of several nitrocelluloses were studied. The ratio of weight-average to number-average molecular weight, determined by viscosity and osmotic pressure measurements, respectively, was taken as a measure of heterogeneity. This ratio is unity for homogeneous material and increases with increasing heterogeneity. The value of the ratio was found to be slightly less than 2 for nitrocelluloses

prepared from cotton linters but was about 2.5 for nitrocelluloses prepared from wood pulp; it is hence concluded that the nitrocelluloses prepared from wood pulp are molecularly more heterogeneous than those from cotton linters.

6.9.5 X-Ray Studies of Nitrocellulose

X-ray diffraction photographs were used to study the degrees of orientation and gelatinization in various smokeless powders.[113,114]

X-ray studies of mixtures of nitrocellulose with diethyl phthalate and with dibutyl phthalate indicated the formation of compounds with these plasticizers.[115]

6.9.6 Studies of Artificially Aged Powders

The techniques described in the preceding sections were used at the California Institute of Technology to study the changes which occur in the nitrocellulose in smokeless powder during accelerated aging at elevated temperatures. These studies indicated that the degradation of nitrocellulose in smokeless powder is very complex. In most of the double-base powders that were heated, a part of the nitrocellulose became insoluble in the customary solvents. The nature of this insoluble material was not established, but it was suspected of being a three-dimensional polymer formed by some sort of cross-linking between nitrocellulose molecules.

6.10 PREPARATION AND PROPERTIES OF SMALL BATCHES OF SOLVENTLESS DOUBLE-BASE POWDER[n]

6.10.1 Introduction

Beginning in July 1942, a comprehensive study of the relationships between the composition and properties of double-base powders was carried on at the California Institute of Technology under OSRD Contract OEMsr-702 (July 1 to December 31, 1942) and OSRD Contract OEMsr-881 (January 1, 1943 to December 31, 1945). An essential tool for this study was the equipment which was developed for the preparation by a slurry method of four-gram batches of rolled solventless sheet powder,[116] and sixty-gram batches of solventless extruded powder.[117]

The equipment for the preparation of four-gram batches of rolled sheet powder is especially suitable for preliminary tests of new compositions. Small samples of highly experimental powders which might be too hazardous to prepare in larger quantity can be prepared with relatively little hazard for small-scale tests, or a wide range of compositions may be quickly surveyed by the preparation of a great many powders of related composition which can then be examined by various means in order to select those most suitable for preparation on a larger scale.

Powders which are to be subjected to surveillance tests, measurements of linear burning rates, or determinations of physical properties, must be prepared in larger lots and in quantities sufficient for extrusion. For this purpose a laboratory was constructed for the mixing, rolling, and extrusion of sixty-gram batches of solventless double-base powder.

These two sets of equipment made it possible to prepare quickly and conveniently a great many powders without which many investigations of propellants would have been impossible; for example, it was feasible to prepare batches of powder which contained no stabilizer or which contained substances which might destabilize the powder.

In the following sections there are briefly described the equipment for preparing small batches of powder and the application of this equipment to studies of the stability, burning rate, and physical properties of standard, new, and foreign propellants.

6.10.2 Equipment for the Preparation of Small Batches of Solventless Double-Base Powders

The equipment which was developed for mixing slurries, the one-inch rolling mill which was designed for rolling four-gram batches of powder, the experimental rubber-rolling mill which was adapted for rolling sixty-gram batches, the one-inch press which was designed to extrude the rolled sheet powder, and the laboratory in which this work was done are described below.

THE LABORATORY

Figure 3 is a plan of the laboratory in which the small batches of solventless powder were prepared. Steam, compressed air, hot and cold water, circulating hot water (190 F), and explosion-proof electrical outlets were supplied at several convenient places in the laboratory. Circulating hot water of constant temperature was supplied from a thermostatically controlled tank from which hot water was

[n]This section is taken from a report prepared by A. O. Dekker.

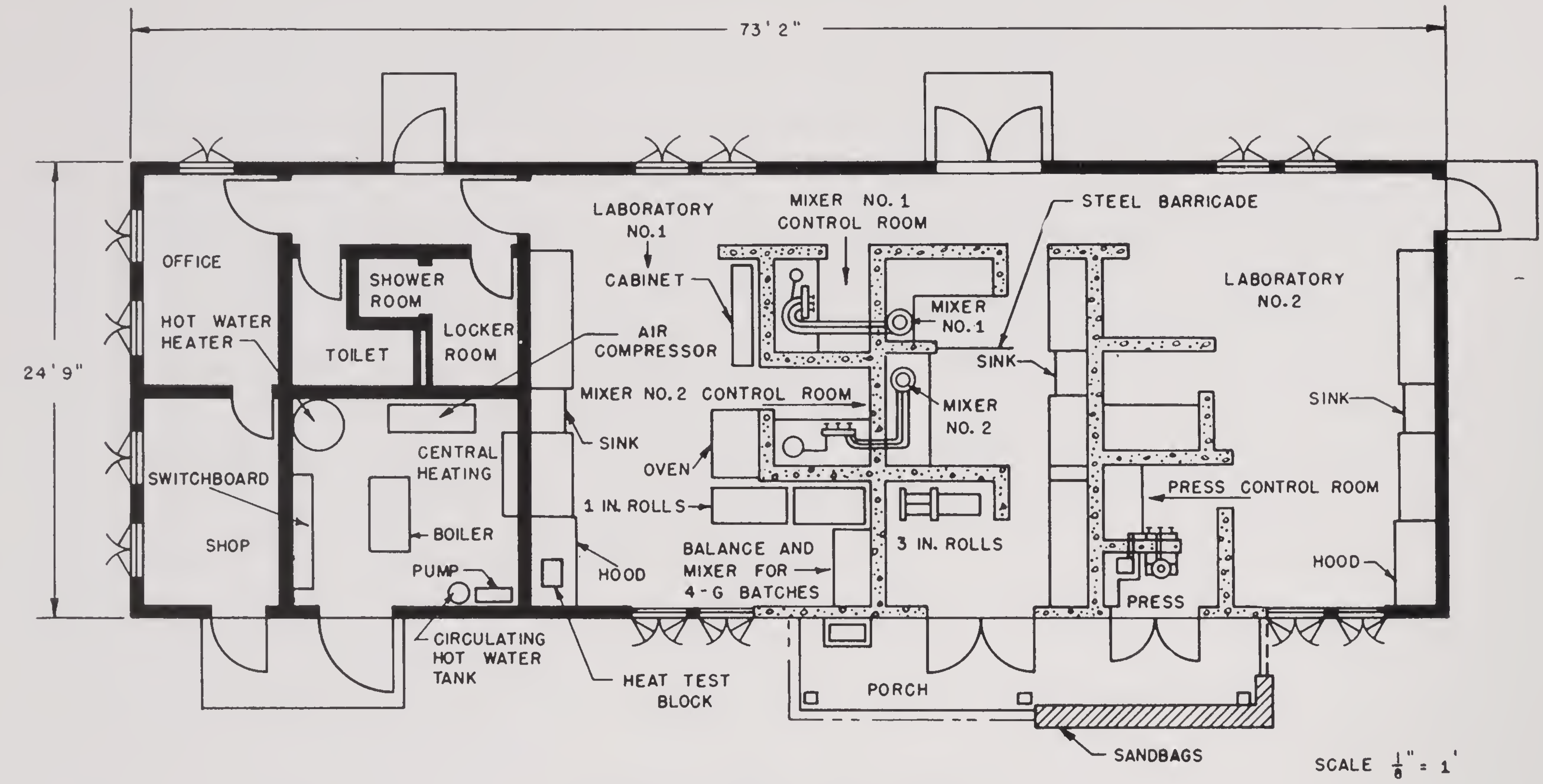

FIGURE 3. Plan of the laboratory.

pumped to the far end of the laboratory by means of a centrifugal pump and was returned to the tank. Apparatus which was to be heated by this circulating water was connected in parallel with the supply and return lines of the system.

Ventilation was provided by several air ejectors which exhausted noxious or explosive vapors at their points of origin.

Emergency showers and fire extinguishers were provided at convenient places throughout the laboratory. Separate magazines for high explosives, nitrocellulose, and double-base powder were situated at appropriate distances from the laboratory.

MIXING THE SLURRY

Slurries for four-gram batches of powder were mixed in small glass beakers which, together with air-driven stirrers and a balance, were mounted behind a steel barricade.

Figure 4 is a photograph of one of the two nearly identical mixers for preparing slurries for sixty-gram batches of powder; this apparatus was designed so that practically all operations were controlled from a panel in another room which was separated from the first by an 8-in. concrete wall. Mirrors permitted the operator to observe the apparatus from the door without exposure. At no time was the operator exposed to high explosives which were at elevated temperatures or in more than gentle motion.

The apparatus is best described by outlining the method of its operation for the preparation of a nitroglycerin powder. A brass cup containing water, and provided with a coil of copper tubing for temperature control was mounted on the piston rod of a hydraulic cylinder. With the piston at its lower position a beaker containing a suitable quantity of a 10% solution of nitroglycerin in alcohol was clamped in the cup. Water at 60 C was passed through the coil in the cup and a brisk stream of filtered air was directed upon the surface of the solution in the beaker. A hood directly above the mixer removed the vapors. When all the alcohol had evaporated, cold

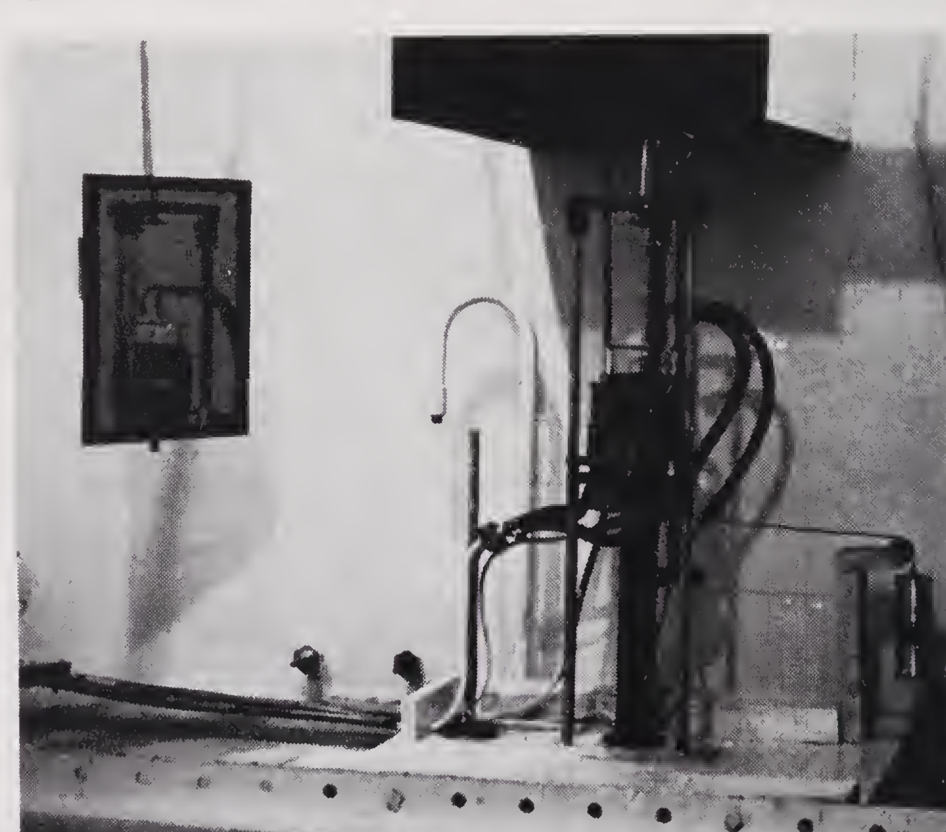

FIGURE 4. Apparatus for mixing sixty-gram batches of double-base powder by a slurry process.

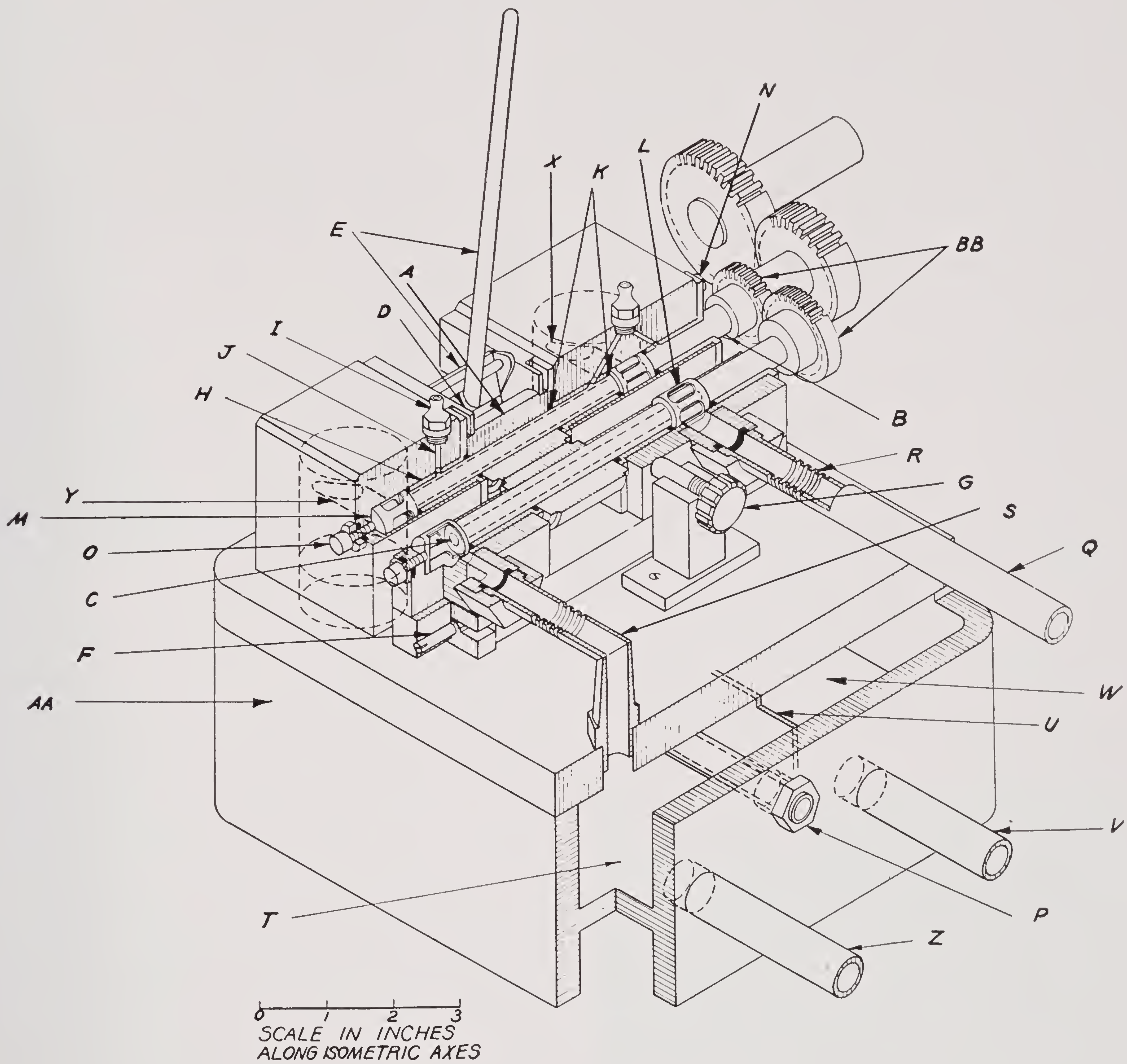

FIGURE 5. Small powder-rolling mill.

AA Iron casting; base of rolls.
BB Interchangeable spur gears.
A Roll (stainless steel collar).
B Roll shaft (stainless steel).
C Central hole in roll shaft, for water circulation.
D Guide; determines width of powder sheet and keeps powder away from bearings.
E Doctor knife for removal of sheet powder from rolls.
F Axle for rotation of block which supports right-hand roll.
G Set-screw for determining space between the rolls.
H Roll-shaft bearing (bronze).
I Lubrication fitting; grease inlet.
J Grease hole.
K Gaskets of "Garlock" packing material (asbestos impregnated with graphite).
L Rear water-circulation bushing (non-rotating).
M Forward water-circulation bushing (non-rotating).
N One of the screws which tighten the rear bearings.
O One of the two screws which tighten the forward bearings.
P Thermometer well.
Q Water-inlet pipe for right-hand roll.
R Flexible metal bellows.
S Outlet pipe from right-hand roll.
T Forward water chamber.
U Partition.
V Water-inlet pipe to rear water chamber and to left-hand roll.
W Rear water chamber.
X Inlet to left-hand roll.
Y Outlet from left-hand roll.
Z Water-outlet pipe, both rolls.

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water was passed through the copper coil, a measured amount of methylcellulose dispersed in water was added to the pure nitroglycerin by remote control, and the cup and beaker were raised by the hydraulic cylinder to the upper position where an air-driven stirrer emulsified the nitroglycerin and water. Nitrocellulose, plasticizer, and stabilizer were then added and the stirring was resumed for 35 minutes.

Slurries containing crystalline explosive plasticizers such as DINA had to be heated above the melting point of the explosive plasticizer during the mixing.

ROLLING THE SLURRIES

One-inch Rolling Mill. The small powder-rolling mill which was designed and constructed in the laboratories of the California Institute of Technology, is shown in Figures 5, 6, and 7. Figure 5 is a cutaway isometric drawing of the mill excluding the motor and worm drive. This drawing shows the details of construction, the bearings and lubrication system, and the water circulation system.

The rolls, which were 1 in. in diameter and $1\frac{1}{8}$ in. long, were driven by a $\frac{1}{8}$-hp explosion-proof electric motor through a worm gear and a set of interchangeable reducing gears; they were mounted on a hollow

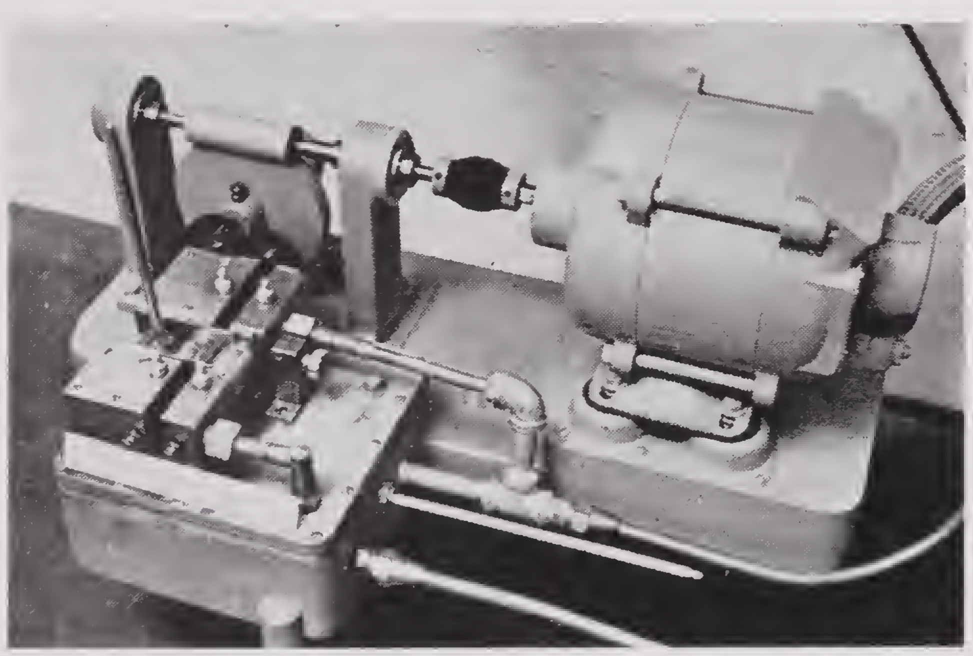


FIGURE 6. Small powder-rolling mill, complete with explosion-proof motor and worm gear.

cast-iron base *AA* by means of which they were supplied with circulating steam or hot water for temperature control. The hot water or steam was caused to flow through the steel shafts which carried the rolls. The spacing between the rolls could be adjusted to any value up to about 0.014 in. by means of an adjustable set-screw *G*. The fast roll was usually driven at a speed of 46.1 rpm and the ratio of the speeds of the two rolls was usually 1.29.

The large angle of nip of the 1-in. rolls caused difficulties which are not encountered with larger rolls. If proper precautions were not taken the stock piled up in the bite of the rolls and did not form a sheet. This difficulty could be avoided by adding the

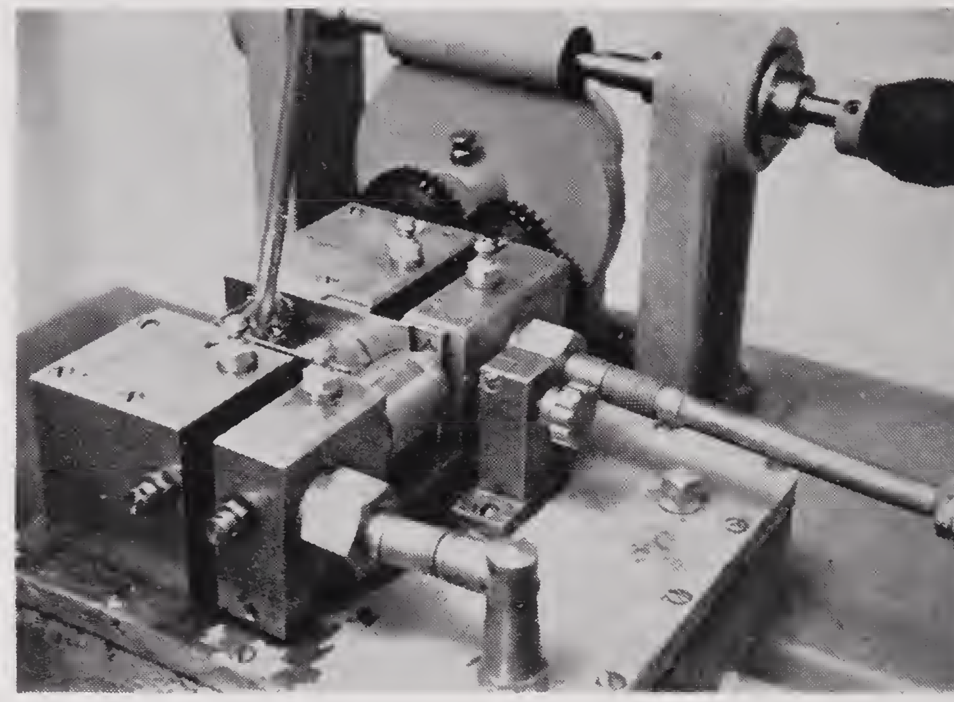


FIGURE 7. Small powder-rolling mill, close-up view.

stock slowly and by carefully controlling the other factors which affect the rolling characteristics of the slurry.

Three-Inch Rolling Mill. The laboratory rubber-rolling mill (Figure 8) was purchased from William E. Thropp and Sons. It consisted of two horizontal heated rolls, 3 in. in diameter and 8 in. long, which were driven by a 2-hp, 3-phase, explosion-proof motor equipped with a magnetic brake. The gears on the front and rear rolls were exchanged so that the front roll would revolve faster than the rear roll. The front roll, which was adjustable for different spacings between the rolls, revolved at 26.9 rpm; the ratio of the speeds of the rolls was 1.40.

The rolls, which were hollow, were connected through suitable valves with the laboratory circulating hot water system, with the cold water and steam lines, and with a heat exchanger, so that the temperature could be regulated as desired. When the proper temperature was reached the rolls were usually spaced at 0.010 in., and the filtered slurry was reduced to a finely divided voluminous mass which was gradually added to the rolls over a period of about half a minute to two minutes, depending on the behavior of the stock on the rolls. The powder was then prerolled for one minute to remove moisture and to initiate plasticization. The partially colloided sheet was bookfolded and returned to the rolls for an additional three minutes, during which the sheet was removed four or five times, folded into several book-

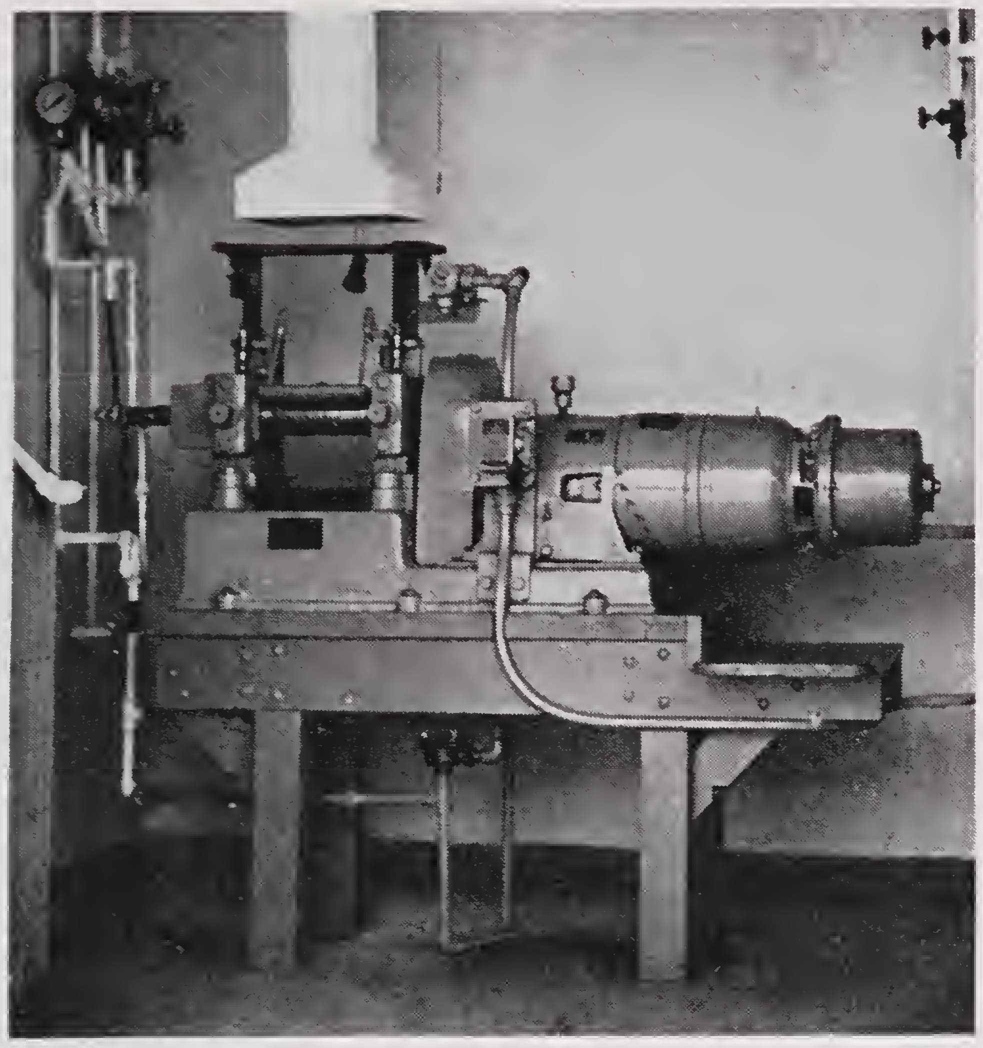


FIGURE 8. Powder-rolling mill, complete with explosion-proof motor and magnetic brake.

folds, and returned to the rolls. Some powders had to be rolled for a longer time as a result of the specific composition or of the condition of the surfaces of the rolls. It was sometimes necessary to reduce the spacing of the rolls in order to plasticize white specks of incompletely incorporated nitrocellulose. Salts and carbon black were added early in this three-minute period.

The sheets obtained were about 6 in. wide, 19 in. long, and of a thickness which was of the order of 0.025 in., but which depended on the quantity of powder which could be conveniently rolled into a sheet.

Extruding the Rolled Sheet Powder

Figure 9 is a drawing in cross section of the barrel and piston of the 1-in. extrusion press, the design of which is based on that of the small 0.5-in. press constructed by Section 5.[o] The barrel of the press, which was machined from heat-treated alloy steel, was mounted vertically and surrounded by a heavy copper heating jacket which contained a helix-shaped water channel; the lower end of the cylinder was threaded to accommodate the die for extrusion. The 1-in. piston, machined from alloy steel and provided with bronze sleeves, was moved by a 10-ton Porto-Power hydraulic ram (Blackhawk Manufacturing Company) which was mounted above and connected to the extrusion cylinder. Provision was made for the evacuation of the press through the piston. A valve in the end of the piston closed the vacuum connection automatically when the piston was pressed against the powder. A second hydraulic cylinder, mounted above the Porto-Power ram and connected to the extrusion piston by four circumferentially spaced connecting rods, withdrew the extrusion piston at the end of its stroke. The two hydraulic cylinders

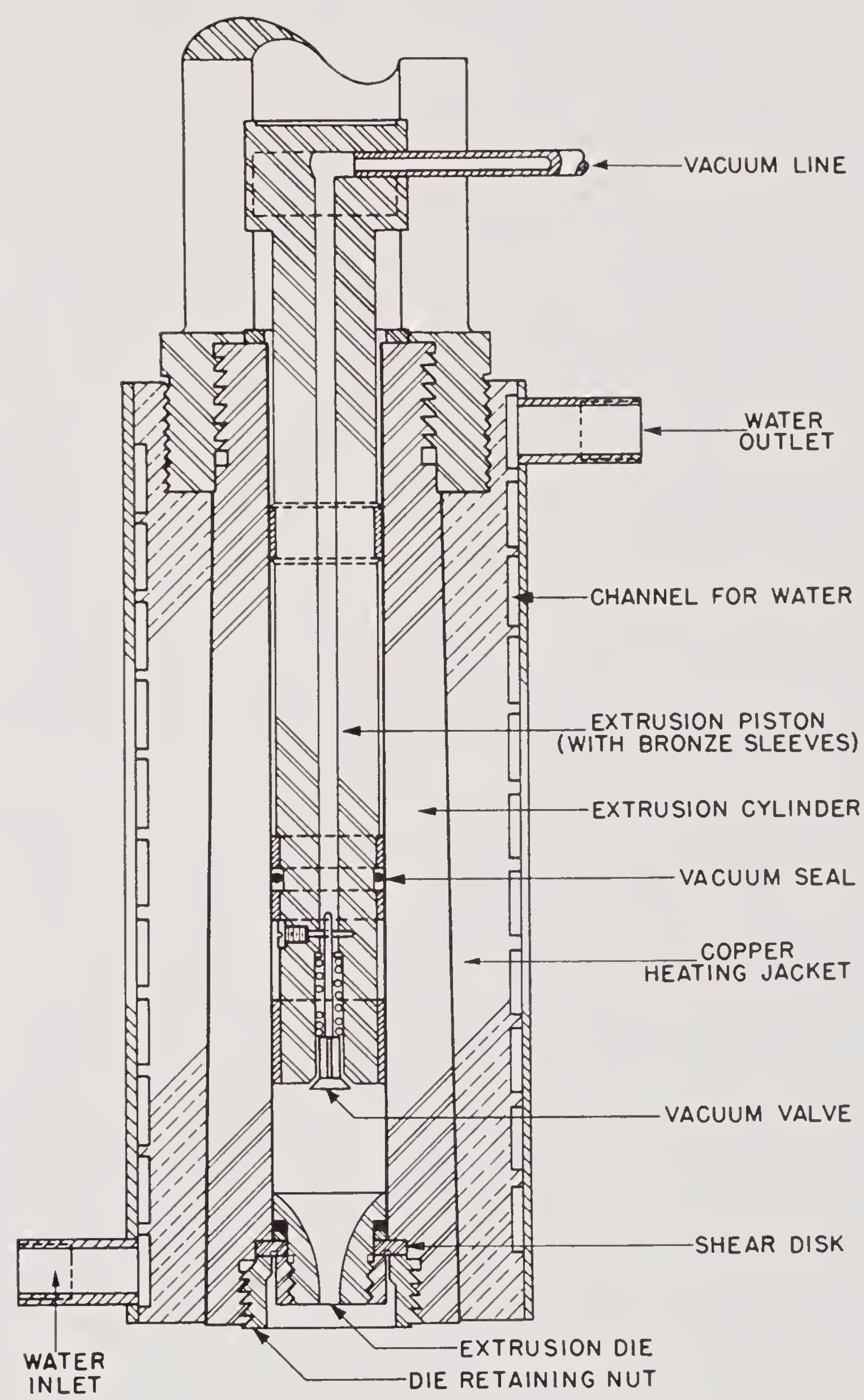


FIGURE 9. One-inch extrusion press, three-quarter size.

were connected by means of a suitable system of valves to a hand-operated pump (Blackhawk Model P-76), to a reservoir, and to a small-capacity accumulator.

Dies for the extrusion of cylindrical rods of powder of $\frac{1}{16}$-, $\frac{3}{32}$-, $\frac{3}{16}$-, $\frac{1}{4}$-, and $\frac{3}{8}$-in. diameter, and spider and mandrels for the extrusion of tubular grains with the dimensions $\frac{3}{8} \times \frac{1}{16}$ in., $\frac{3}{32} \times \frac{1}{32}$ in., and $\frac{3}{32} \times \frac{1}{64}$ in. were prepared according to the meth-

[o]Contract OEMsr-418.[118a]

[redacted]

ods of design which were developed by Section 5.[p]

The 1-in. press proved to be very satisfactory with the exception of the hydraulic system. A more easily controlled and operated hydraulic system which would deliver a more nearly constant pressure probably could be assembled from a double-acting cylinder and a motor-driven pump which can be purchased on the market, but this hand-operated pump and the two single-acting cylinders were fairly satisfactory.

Preliminary to extrusion the sheet obtained from the 3-in. rolls was formed into a tight carpet roll 6 in. long and nearly an inch in diameter. The carpet roll was preheated at a suitable temperature for 20 minutes and then placed in the press at the same temperature. The press was evacuated for two minutes at 4 mm of mercury pressure and the extrusion was started. The pressure prevailing during the extrusion was of a magnitude such that the rate of extrusion of a quarter-inch grain was of the order of an inch per second, and correspondingly higher pressures and rates were used for smaller granulations; no effort was made to obtain any particular extrusion rate.

Discussion of the Procedure for the Preparation of Small Batches of Powder

Effect of Variations in the Mixing and Rolling Procedures. An extensive series of experiments was carried out in order to determine the extent to which the properties of four-gram batches of powder were affected by variations in the procedure such as those which were to be expected under ordinary operating conditions. The time and violence of mixing the slurry, the moisture content of the slurry at the time of placing it on the rolls, the time and temperature of rolling on the 1-in. rolls, and many other variables were investigated. The variations had either no effect or an insignificantly small effect on the rolling characteristics of the slurry, and on the qualitative physical properties, the *p*H value, and the vacuum stability behavior of the powders.

Comparison of Batch Formulas and Analyses. Many four-gram and sixty-gram batches of powder were prepared and analyzed in order to determine the precision with which the compositions of the experimental powders could be controlled. These analyses permitted the development of precise procedures for the preparation of powders, so that their compositions were generally closer to the specifications than was the practice with production lots of powder.

Comparison of Powders with Production Lots. In appearance, qualitative physical properties, and burning rate, the sixty-gram batches of powder could not be distinguished from production lots of identical composition.

In stability there seemed to be no significant differences between the small batches and production lots except for diphenylamine-stabilized powders. For example, without exception the centralite-stabilized powders prepared at the California Institute of Technology, when stored at elevated temperatures, were depleted of centralite at rates which could have been predicted roughly from the rates of depletion in production lots of similar composition.[119] On the other hand, also without exception, the diphenylamine-stabilized powders, which were prepared in this laboratory, were depleted of diphenylamine more than twice as rapidly as ballistites which were prepared in production lots.[120]

Investigation showed that this anomalous behavior of the diphenylamine powders was to be ascribed only to the operations of rolling the powder on the 3-in. rolls and extruding the powder from the 1-in. press and not to the mixing of the slurry or to the purity of the components of the slurry. It is possible that this behavior was due to air taken up by the powder during rolling and extrusion.

Quantity of Production. One man was able to mix and roll 10 four-gram batches of different compositions in three eight-hour days. This output could be doubled if the laboratory were in a plant where nitroglycerin is manufactured so that pure nitroglycerin could be obtained without the time-consuming evaporation of alcohol from a 10% solution.

Two men were able to mix, roll, and extrude about 20 or 25 sixty-gram batches of powder in five eight-hour days; however, if the compositions were not very closely related, so that the rolling or extrusion conditions had to be changed for each batch, the number of batches produced in this time was only a dozen or so. Here again the output could be doubled if pure nitroglycerin rather than a solution were available. Moreover, a different plan for the building and for the location of operations in it would permit perhaps a 30% increase in output, even though only nitroglycerin solutions were available; with the present arrangement it was not considered safe to permit powders to be rolled at the same time that other powders were being mixed in the adjoining room.

[p]Contract OEMsr-418.[118b]

6.10.3 Application of the Equipment to Studies of Smokeless Powder

The equipment for the preparation of four-gram batches was used to prepare about 700 batches of powder for studies of various plasticizers and stabilizers, for studies relating to the formulation of new propellants, and for investigation of foreign propellants. The equipment for the preparation of sixty-gram batches was used to prepare more than 500 batches of powder for similar studies and for use in determinations of the linear burning rate and elastic modulus of propellants under compression.

The slurry mixer, 3-in. rolls, and 1-in. press, described in the preceding sections, were not only useful but essential to the prosecution of the work on this contract. The more significant types of investigations which were made with this equipment and with the smaller equipment are indicated very briefly in the following sections.

Comparison of Various Compounds as Plasticizers in Solventless Rolled Sheet Powder

Nonexplosive Plasticizers. The 1-in. rolls were originally intended for use in a study of the relative merits of a wide variety of compounds as plasticizers of nitrocellulose in solventless powders. A description of the general procedure used in these investigations is given in the following paragraphs, and a summary of the results obtained is presented in Table 3.

All the powders were based on a ballistite composition and contained neither salt nor coloring agent. Four-gram batches of powder containing 3 to 5% of each plasticizer alone were mixed, the powders were rolled on the 1-in. differential rolls at 75 C by a standard procedure, and the length of time required for each mix to form a translucent sheet was noted as a criterion of the rate of plasticization of the nitrocellulose. The finished sheets were examined visually and were rubbed and flexed with the fingers; small pieces were pulled off and torn from the sheet to obtain some indication of the toughness of the sheets.

The results of studies of several series of plasticizers are summarized roughly in Table 3. Many of the 89 compounds listed were studied while the technique of rolling sheet powders on the 1-in. rolls was still being developed; the classification of these compounds is somewhat uncertain, and they are marked with an asterisk to distinguish them from the compounds which have been studied more recently.

TABLE 3. Tentative classification of various compounds as plasticizers of nitrocellulose in solventless rolled sheet powders.[116,121]

Group I *Compounds which yield flexible sheet powders*	
Acetophenone*	Diphenylformamide
Allyl 2-nitro-2-methylpropyl maleate	Diphenylurethane
	Ethyl centralite
Butyl lactate*	Ethylphenylformamide
Butyl phthalyl butyl glycolate*	N-Ethyl-N-phenylurea
Cyclohexanone*	Isophorone*
Dibutyl phthalate*	Pentaerythritol diacetate dipropionate
Diethoxyethyl phthalate*	
Diethyloxanilide	Pentaerythritol tetraacetate
Diethyl phthalate	Phthalide
Diethyl tartrate	*o*- and *p*-Toluene ethyl sulfonamides*
Di(2-nitro-2-methylpropyl) maleate	
	o- and *p*-Toluene sulfonamides*
Diphenylcarbamic anhydride	Triacetin
	Triethyl citrate*
Group II *Compounds which yield stiff sheet powders*	
Acardite	Methyl phthalyl ethyl glycolate
Acetyl tributyl citrate*	Sucrose octaacetate
Dimethoxyethyl phthalate	Tetraphenylurea†
Diphenyloxanilide	Tricresyl phosphate
N-Ethyl-N′-phenylurea†	Triphenylisocyanuric acid
Group III *Compounds which yield poorly plasticized, weak, brittle sheet powders*	
Dibutyl sebacate*	Methyl abietate*
Hexaphenylmelamine	β-Nerolin

*Studied during the preparation of the first 75 powders on the 1-in. rolls
†Several days after rolling, the surfaces of sheets containing 4.25% of this compound exhibited microscopic crystals.

Explosive Plasticizers. A qualitative comparison of the plasticizing actions of diethylene glycol dinitrate and nitroglycerin in ballistite JPH was made by means of the 3-in. rolls and 1-in. press.[122]

Sixty-gram batches of powders of the compositions shown in Table 4 were mixed and rolled and then extruded through a 0.25-in. die.

DEGN, which softened the powder much more than nitroglycerin, is apparently best suited to the preparation of powders which contain a larger percentage of nitrocellulose.

The two powders prepared from pyrocotton seemed to be harder than those prepared from the blend of pyro- and guncotton. Preliminary quantitative measurements of the hardness of nitroglycerin powders with a testing machine (Section 6.13) indicated that this effect of the nitrogen content of the nitrocellulose was real.

The study of the plasticization of powders by explosive and nonexplosive plasticizers was better carried out on the sixty-gram scale than on the four-gram scale, because additional data were obtained during the extrusion and because quantitative deter-

TABLE 4. Composition and qualitative physical properties of powders containing nitroglycerin (NG) or diethylene glycol dinitrate (DEGN).

a. *Formula percentage composition*

Nitrocotton	54.5
Explosive plasticizer	43.0
Ethyl centralite	1.00
Potassium sulfate	1.50
Carbon black (added)	0.10

The types of nitrocotton and explosive plasticizer are listed below.

Powder No.	C-112	C-113	C-114	C-115
Nitrocotton, Lot No.	5251	10411	5251	10411
Per cent of N	12.55	13.23	12.55	13.23
Viscosity (Hercules seconds)	10	11	10	11
Explosive plasticizer	NG	NG	DEGN	DEGN

b. *Qualitative physical properties of grains extruded through a 0.25-in. die*

Powder No.	C-112	C-113	C-114	C-115
Extrusion pressure (psi)	6100	4600	3100	2300
Average diameter (inch)	0.278	0.272	0.273	0.269
Hardness	Very hard	Hard	Soft	Very soft

minations of the hardness and elastic modulus under compression could be made with the extruded powders.

Relationship Between the Properties of the Nitrocellulose and the Strength of JPH-Type Ballistites

As indicated in the preceding paragraphs, sixty-gram batches of powder are suitable for studies of the relationship between the properties of the nitrocellulose and the strength of the powder in which these nitrocelluloses are incorporated. In an investigation which was designed to develop a new propellant with greater physical strength than ballistite JPH, 16 powders were prepared which were identical in composition except for the nitrocellulose which was used, and the hardness and elastic modulus under compression of each of these were to be determined. The compositions of these powders are shown in Table 5. This type of investigation could be carried out more economically and expeditiously by the use of the laboratory for the preparation of small batches of powder than by use of a pilot plant in which batches of at least several hundred pounds are usually made.

Studies Which Relate to the Stability of Double-Base Powder

The investigations carried out under OSRD Contract OEMsr-881 were largely concerned with the study of the stability and safe life of double-base powders. In connection with these investigations, a vacuum stability test at 110 C and a modified Taliani test at 110 C were developed for use with double-base powders (Section 6.12). These tests were applied to a study of the effects of a great variety of changes in composition upon the relative rates of gas evolution. Powders prepared in small batches in this laboratory provided the material from which many data were obtained for investigation of relationships between the composition and the stability of double-base powders.

The apparatus for the preparation of sixty-gram batches of powder was more suitable than the smaller equipment, because forty-five-gram samples of the larger batches were available for surveillance tests and ten- to fifty-gram samples could be stored for determination of the rate of depletion of the stabilizer. In this way data could be obtained to test the validity of correlations between the long-time low-temperature tests, such as the standard surveillance test at 65.5 C, and the short-time high-temperature tests, such as the Taliani-type test.

TABLE 5. Formula percentage composition of JPH-type ballistites which contain different nitrocelluloses.

Nitrocellulose, according to specifications below	54.5
Nitroglycerin	43.0
Ethyl centralite	1.00
Potassium sulfate	1.50
Carbon black (added)	0.10

Powder No.	Description of Nitrocellulose: Hercules Lot No.	Nitrogen per cent	Viscosity, Hercules seconds	Type
C-137	5168	12.60	8	Cotton
C-138	8432	12.67	8	Wood
C-139	5250	12.55	15	Cotton
C-140	5245	12.52	15	Wood
C-171	2917	11.89	11.7	Cotton
C-172	2733	11.98	6.0	Cotton and wood
C-173	2936	12.13	1.0	Cotton and wood
C-174	3293	11.95	0.49	Cotton and wood
C-175	1087	11.95	0.04	Wood
C-211	5247	13.45	11	Cotton
C-213	2917 (27.25%)	11.89	11.7	Cotton
	3323 (27.25%)	12.08	0.04	Cotton and wood
C-214	3323 (15.6%)	12.08	0.04	Cotton and wood
	5250 (38.9%)	12.55	14	Cotton
C-215	2733 (30.5%)	11.98	6.0	Cotton and wood
	5247 (24.0%)	13.45	11	Cotton
C-216	2917 (30.0%)	11.89	11.7	Cotton
	5247 (24.5%)	13.45	11	Cotton
C-217	3234 (18.3%)	10.96	0.05	Cotton
	5246 (36.2%)	13.45	13	Cotton
C-218	1087 (37.1%)	11.99	0.04	Wood
	2465* (17.4%)	13.96	100	Cotton

*This lot was prepared at the Picatinny Arsenal.

The equipment was used to prepare powders in which different explosives, nitrocelluloses, coloring agents, plasticizers, stabilizers, and various organic and inorganic compounds were incorporated, and the powders were investigated by means of the tests which have already been mentioned.

For example, nine powders of JPH-type composition were prepared, in which the following stabilizers or compounds were used respectively.

No stabilizer	Diphenylurethane
Ethyl centralite	Carbazole
Diphenylformamide	β-Nerolin
Acardite	Tetraphenylurea
Ethylphenylurethane	

Samples of the powders were placed in surveillance at 65.5 C and at 75 C, and vacuum stability and Taliani tests were made on the other samples.

As another example, powders containing as stabilizers those derivatives of diphenylamine or ethyl centralite which are formed during the decomposition of the powder were prepared for use in studies of the kinetics of the reactions which are involved in the decomposition of the powder at 65, 71, or 75 C. For this purpose 14 ballistite-type powders containing the following respective stabilizers were prepared.

Diphenylamine	N-Nitroso-4-nitrodiphenylamine
N-Nitrosodiphenylamine	Ethyl centralite
4-Nitrosodiphenylamine	4-Nitrocentralite
2-Nitrodiphenylamine	N-Nitroso-N-ethylaniline
4-Nitrodiphenylamine	N-Nitroso-4-nitro-N-ethylaniline
4,4′-Dinitrodiphenylamine	4,4′-Dinitrocentralite
2,4,4′-Trinitrodiphenylamine	
2,2′,4,4′,6,6′-Hexanitrodiphenylamine	

The rates of transformation of these stabilizers at elevated temperatures were determined.

Investigations of the Linear Burning Rates of Propellent Powders of Various Compositions

The apparatus for the preparation of sixty-gram batches of powder played a necessary part in investigations of the linear burning rates of propellent powders[123] which were carried out under OSRD Contract OEMsr-881. Every powder whose burning rate was to be determined had to be provided in a granulation suitable for use in the burning rate apparatus. Samples from production lots or pilot lots of American powders, and samples of captured German and Japanese powders were reduced to $\frac{3}{32}$-in. grains by use of the rolls and the press. Powders prepared from our own slurries were also extruded as $\frac{3}{32}$-in. grains.

In addition to this function of supplying material in a suitable granulation, the laboratory made it possible to carry out studies of the relationships between the composition of powder and its burning characteristics. For example, it was reported[124,125] that one of the new standard compositions for use in German rockets was the one listed in Table 6.

Table 6. Percentage composition of German Einheitspulver R 61

Nitrocellulose (12.5 per cent nitrogen)	59.8
Diethylene glycol dinitrate	35.3
Hydrocellulose	1.50
Ethylphenylurethane	1.10
Diphenylurethane	0.80
I. G. Wax E	0.35
Magnesium oxide	0.20
Potassium nitrate	0.60
Acardite	0.30

In the absence of a captured sample of this composition, a sixty-gram batch was prepared in which was incorporated 0.10% of graphite, while carnauba wax was substituted for the I. G. Wax E. Measurement of the burning rates at various temperatures and pressures showed that this powder had a lower temperature coefficient of the linear burning rate and a lower pressure coefficient of the linear burning rate than any of the other powders containing diethylene glycol dinitrate which were investigated at the California Institute of Technology. To determine the cause of these superior burning properties, about 40 additional powders were prepared in which various constituents were omitted or replaced by closely related substances. By this means it was possible to show that the combination of hydrocellulose and potassium nitrate (and, to a lesser extent, magnesium oxide) produced superior burning characteristics. It was also possible to show that incorporation of these substances had little or no effect on ballistite but improved the burning characteristics of H-4 powder. A study of this sort by means of 500-lb pilot-lot batches would have been much more expensive and time-consuming.

Foreign Propellants

As indicated in the preceding section, the equipment was useful in studying the linear burning rates of foreign propellants. Not only was it possible to investigate the detailed features of the burning characteristics of captured foreign powders, but it was also possible to test the validity of quantitative analyses of these propellants. When the composition was determined by analysis, a sixty-gram batch of powder could be prepared for a comparison of its physical

properties and burning characteristics with those of the foreign powder.

New Propellants

Some of the applications of the equipment for the preparation of small batches of powder to the development of new propellants are partly evident from the preceding sections on studies of plasticization, nitrocellulose, stability, and linear burning rates. In addition to the types of investigations which have already been indicated, several other series of experiments were made with a view to the formulation of new propellants. The results of two of these series are very briefly described in the following paragraphs.

RDX and PETN Propellants. Powders of relatively high potential, in comparison with a JPH-type ballistite, were prepared in four-gram batches by the incorporation of RDX and PETN in a ballistite-type binder. Powders containing as much as 36% of PETN in a ballistite matrix, and with heats of explosion as much as 100 calories per gram higher than that of JPH, were prepared, and their qualitative physical properties were determined.[126] The sheets were fairly flexible, but contained small perforations and, upon aging, crystals developed on the surfaces. The experiments were not continued.

DINA Propellants. Because of the relatively high volatility of nitroglycerin, there was considerable interest in the development of new propellants which contain less volatile explosive plasticizers. For this work the 1-in. rolls provided a very convenient and economical method of determining whether or not projected compositions could be successfully colloided by solventless rolling, and for obtaining samples for qualitative comparisons. A comprehensive study of powders containing DINA, Fivonite, and methyl NENA was carried out with this equipment. Four-gram batches of more than fifty different compositions were prepared, qualitative observations were made of their physical properties, and some were tested in the vacuum stability apparatus.[85] Fivonite was found to be useful in relatively small quantities as a plasticizer for DINA powders; when used as the only explosive plasticizer in a powder, Fivonite yielded a slurry which could not be rolled. Methyl NENA offered no advantages over Fivonite as a plasticizer for DINA powders and had the disadvantage of being about as volatile as nitroglycerin.[127] All the powders which had ballistic properties comparable to those of ballistite were supersaturated with respect to the explosive plasticizer, and this crystallized on the surface of the sheets on standing. As in Albanite gun propellants, it was by no means certain that the crystallization was a serious disadvantage, but this could only be determined by much more extensive investigations.

6.11 THE ANALYSIS OF POWDERS[q]

6.11.1 Chemical and Physical Methods

The material presented in this section is primarily the result of work carried out at the California Institute of Technology under OSRD Contract OEMsr-881. It consists essentially of critical investigations of many of the standard methods currently used for the determination of individual constituents of smokeless powders and of new or revised procedures which were developed for the analysis of new powders or for the attainment of greater precision. In addition to these purely analytical problems, studies have been made of the fractionation, molecular weight determination, and aging behavior of nitrocellulose; these studies are described in Section 6.9.

The analytical investigations and procedures are grouped for discussion under the following headings:

1. Procedures for the determination of nitrocellulose and for the estimation of the percentage of nitrogen in it.
2. Procedures for the identification and quantitative estimation of nitric esters and nitro compounds.
3. Procedures for the quantitative estimation of stabilizers and nonexplosive plasticizers.
4. Procedures for the quantitative estimation of volatile and inorganic constituents.

The application of chromatographic and spectrophotometric methods to problems of powder analysis is described in Section 6.11.2.

Procedures for the determination of Nitrocellulose and for the Estimation of the Percentage of Nitrogen

All analytical studies of nitrocellulose from powder are hampered by the difficulty of obtaining samples of nitrocellulose which are free from moisture and volatile solvents, and are in a form suitable for further study. Samples of commercial uncolloided water-wet nitrocellulose can be dried easily, either by mild heating or by vacuum desiccation, but material which

[q] This section is taken from a report submitted by Richard M. Noyes.

has been precipitated from dispersions in organic solvents can be dried only with difficulty and is apparently degraded by heat more easily than is untreated nitrocellulose.

Determination of Nitrocellulose. Nitrocellulose in smokeless powder is customarily determined in the residue remaining after extraction of the sample with ether or methylene chloride. The solvent retained in the residue after extraction cannot be removed by gentle heating or evacuation, but two procedures are available for obtaining the nitrocellulose in a form suitable for weighing.

The usual procedure, called the Naval Powder Factory procedure, is that embodied in the specifications for the analysis of JPN powder.[128a] It involves dispersing the nitrocellulose in 2/1 ether-alcohol, evaporating part of the ether, and precipitating the nitrocellulose with water. The resulting mixture is then evaporated, and the residue is dried to constant weight.

An alternative procedure involves dispersing the nitrocellulose in acetone, and precipitating it by pouring the acetone solution into a large volume of a dilute aqueous solution of sodium chloride. The precipitate is then filtered on a sintered-glass funnel, washed with water, and dried to constant weight.

The Naval Powder Factory procedure has given quite satisfactory results for the analysis of most smokeless powders, but the molecular weights of nitrocelluloses are markedly decreased by this treatment. The procedure involving solution in acetone, precipitation, and filtration is to be preferred for the analysis of powders containing a considerable amount of water-soluble inorganic salt which must be separated before the nitrocellulose can be determined accurately. A method utilizing this procedure was developed for the analysis of EJA powders.[69]

Estimation of Nitrogen in Nitrocellulose. The du Pont nitrometer is customarily used for the estimation of nitrogen in nitrocellulose,[109] it has proved to be entirely satisfactory for the analysis of dried one-gram samples of commercial nitrocellulose; however, low results have sometimes been obtained with samples that had been subjected to the Naval Powder Factory procedure described above. Those nitrocelluloses which gave low results contained 12.6% or less of nitrogen and were almost completely soluble in 2/1 ether-alcohol; they formed gelatinous precipitates when water was added and dried to "horny" lumps. If an attempt was made to dissolve these samples in sulfuric acid before the resulting solutions were shaken in the nitrometer, the results were improved but were not always satisfactory. Therefore the nitrometer, although it is the most accurate procedure for the estimation of nitrogen in commercial nitrocellulose, cannot be recommended for the analysis of samples that have been colloided with solvent and then precipitated.

A Devarda procedure has also been employed for the estimation of nitrogen in 0.1-g samples of nitrocellulose.[129] This procedure involves hydrolysis of the nitrocellulose in a solution of sodium hydroxide and hydrogen peroxide, reduction of the nitrate ion with Devarda's alloy, and distillation and titration of the resulting ammonia. This procedure has given very satisfactory results for the analysis of samples of commercial nitrocellulose. Like the nitrometer, the Devarda procedure gave low results for the analysis of some samples of precipitated nitrocellulose, but a modification of this procedure[130] in which sodium peroxide is substituted for hydrogen peroxide was found to give results accurate within about one-half per cent of the nitrogen present. The modified Devarda procedure is recommended for the estimation of nitrogen in samples of commercial nitrocellulose, when less than one gram is available and in samples of precipitated nitrocellulose.

Several attempts were made to estimate nitrogen in nitrocellulose by reduction with ferrous chloride and estimation of the resulting ferric ion by a procedure similar to that used for the determination of nitroglycerin discussed below. The results were unsatisfactory.

Procedures for the Identification and Quantitative Estimation of Nitric Esters and Nitro Compounds

Identification by X-ray Diffraction. X-ray diffraction powder photographs are of considerable assistance in identifying unknown crystalline constitutents encountered in explosives. In order to aid in this identification, X-ray photographs have been taken of several crystalline explosive constituents of propellants, and tables of interplanar spacings and diagrams illustrating the relative positions and intensities of the observed reflections have been collected.[131] Among the substances for which data are presented are the following explosives: PETN, 4,6-dinitrotoluene, TNT, picric acid, ammonium picrate, guanidine picrate, Haleite, nitroguanidine, Fivonite, DINA, RDX, β-HMX, and QDX (SEX).

Analysis by Chemical Procedures. The most satis-

factory procedure for the estimation in a powder of nitric esters, other than nitrocellulose, involves the titration of ferric ion with a solution of titanous chloride. A sample of the powder is extracted and the solvent is evaporated from the extract, the residue from the evaporation is dissolved in glacial acetic acid, and an aliquot portion of this solution is then reduced by a mixture of ferrous chloride and hydrochloric acid, and the resulting ferric ion is titrated with a standard solution of titanous chloride with the use of ammonium thiocyanate as indicator.[128b,132,133]

This procedure has been found to be entirely satisfactory for the determination of nitroglycerin and of diethylene glycol dinitrate in smokeless powder.

It has been found that the detectable nitroglycerin in extracts of JPN-type powder decreased with time if the solutions to be analyzed are allowed to stand either in ether or in glacial acetic acid. Storage of extracts for longer than one day is not advisable; but if storage is necessary, the rate of the apparent deterioration of the extract can be decreased by low temperature.[134]

No attempts were made to analyze powders containing pentaerythritol tetranitrate, but analyses of a purified sample of this explosive by the procedure described above were low by approximately one per cent.[135]

Fivonite (2,2,5,5-tetramethylolcyclopentanone tetranitrate) and DINA (diethanolnitramine dinitrate) could not be titrated quantitatively by the standard procedure, but satisfactory results were obtained if 2.0 *N* ferrous chloride was substituted for the usual 0.7 *N* solution.[136] Only the nitric ester groups in DINA are reduced under these conditions; the nitramino group is apparently unaffected. Satisfactory results were obtained for the analysis of powders of modified Cordite N composition which contained these explosives.[137]

Nitroguanidine was slowly reduced under the conditions described above, but the results of a few preliminary experiments were not quantitative.[138] Since nitroguanidine is somewhat soluble in ether, it may interfere with the estimation of nitric esters by the usual procedure. Therefore, powders containing this substance should be extracted with carbon tetrachloride instead of with ether. The only nonchromatographic procedure studied at the California Institute of Technology for the determination of nitroguanidine in smokeless powder was a gravimetric British procedure based on the loss in weight resulting from extraction with hot water.[139]

Dinitrotoluene supposedly is not reduced by ferrous chloride in the presence of nitroglycerin, but it can be determined by reduction with an excess of titanous chloride and back titration with a standard solution of ferric alum. This procedure has been found to be quite satisfactory for the determination of dinitrotoluene in FNH powder.

The titanous chloride solution used in the titrations described above is customarily standardized against ferric ion obtained by oxidizing a known quantity of Mohr's salt. The procedure described in the government specifications involves oxidizing the sample of Mohr's salt by titrating it with permanganate to the usual end point. A more rapid and equally satisfactory procedure is to oxidize the sample with bromine and to boil off the excess bromine before titration with titanous chloride.

Procedures for the Quantitative Estimation of Stabilizers and Nonexplosive Plasticizers

The results of studies on nonchromatographic procedures for the determination of stabilizers and nonexplosive plasticizers incorporated in American and foreign propellants are presented below. Because of the differences in the chemical properties of these constituents, the material has been organized according to substances instead of according to procedures as in the preceding section.

Determination of Centralite. The customary chemical procedures for the determination of centralite in smokeless powder involve bromination to dibromocentralite. Gravimetric procedures[140-144] which are now in use are more time-consuming than volumetric procedures, and therefore have not been used extensively in this country. The two volumetric bromination procedures which are in common use are the carbon tetrachloride procedure of the Hercules Powder Company[128c] and the alcohol procedure of the Naval Powder Factory and the Picatinny Arsenal.[128d] In each procedure the sample to be analyzed is dissolved in the specified solvent and is treated with a known excess of a standard solution of bromate-bromide. An excess of hydrochloric acid is added, and the centralite is brominated by the bromine which is liberated. An excess of potassium iodide is then added, and the iodine which is produced is titrated with a standard solution of thiosulfate. The carbon tetrachloride procedure gives very satisfactory results, but the manipulations are somewhat cumbersome because the two-phase system must be shaken vigorously during the bromination and also during titration. The technique

of the alcohol procedure is easier because the bromination and titration are carried out in a one-phase system, but the time and temperature of bromination must be controlled carefully in order to avoid errors due to bromination of the solvent. The advantages of both procedures can be combined in a one-phase system which is inert to bromine if glacial acetic acid is used for the organic solvent. The details of the acetic acid procedure and the results of the analyses of representative powders by it are presented in a formal report.[145]

Powder samples which are to be analyzed for centralite by volumetric bromination procedures should not be extracted with diethyl ether, because peroxides in the ether may interfere with the subsequent analysis of the extract.[146]

Extracts of JPN powders can be stored at room temperature for at least two weeks in methylene chloride, or in glacial acetic acid without apparent decrease in the amount of centralite detected by volumetric bromination.[147]

X-ray diffraction data for the identification of ethyl centralite have been obtained.

Determination of Diphenylamine. Three quite different procedures are in general use for the estimation of diphenylamine in smokeless powder: the nitric acid-digestion procedure for the estimation of "total" diphenylamine, the soda-distillation procedure for the estimation of "available" diphenylamine, and the chromatographic-spectrophotometric procedure for the estimation of "actual" diphenylamine. Critical studies have been made of each of these procedures.[148]

The nitric acid-digestion procedure[149] involves the digestion of a powder sample with a mixture of nitric and acetic acids under conditions which lead to almost complete nitration of the stabilizer to hexanitrodiphenylamine, which is estimated gravimetrically. Since not only the unreacted diphenylamine but also all of the partially nitrated derivatives are estimated by this procedure the result is reported as total diphenylamine. This procedure is satisfactory for the purposes for which it is intended.

The soda-distillation procedure for the estimation of available diphenylamine involves the decomposition of the powder with aqueous sodium hydroxide and the distillation of the resulting mixture with steam. The distillate is then extracted, and the extract is analyzed for diphenylamine by gravimetric or volumetric bromination procedures. It is claimed that any N-nitrosodiphenylamine is converted to diphenylamine under the conditions of the soda distillation and is ultimately estimated as such. Since N-nitrosodiphenylamine is also thought to exert a stabilizing action on the powder, the soda-distillation procedure may be said to measure the total percentage of diphenylamine and derivatives available for stabilization.

Subsequent studies have indicated that the soda-distillation and gravimetric bromination procedures determine the approximate total amount of diphenylamine and N-nitrosodiphenylamine in a powder sample, but that the results tend to be somewhat low. The volumetric bromination procedure is not satisfactory for the analysis of distillates from powders containing a considerable amount of N-nitrosodiphenylamine, but British workers[150] claim that results agreeing with those from gravimetric bromination can be obtained if the distillate is reduced with titanous sulfate before it is extracted and analyzed.

The chromatographic procedures described below for the estimation of actual diphenylamine and of diphenylamine derivatives are recommended if it is desired to estimate the percentages of unreacted diphenylamine and of partially nitrated products in a sample of smokeless powder.

Ether peroxides interfere with the volumetric determination of diphenylamine just as they do with that of centralite.

X-ray diffraction data for the identification of diphenylamine and of some of its partially nitrated derivatives have been obtained.

Determination of Diethyl Phthalate and Dibutyl Phthalate. The digestion procedure involving saponification of phthalate esters during digestion of the powder with nitric acid, precipitation of lead phthalate, and estimation of lead in the precipitate as lead sulfate[128e,151] is tedious but is claimed to give reproducible results in the hands of an experienced operator.

In addition to the chromatographic-spectrophotometric procedure described in Section 6.11.2, a procedure involving chromatographic separation and gravimetric estimation has been developed at the Radford Ordnance Works.[152] Attempts at the California Institute of Technology to develop a procedure involving chromatographic separation and volumetric estimation were promising but were not carried to completion.[153]

Determination of Urethanes. Some attempts were made to develop chemical procedures for the estimation of ethylphenylurethane and diphenylurethane. These substances did not absorb bromine directly but

could be hydrolyzed with alkali under drastic conditions to ethylaniline and diphenylamine, respectively; these hydrolysis products could then be estimated by bromination. Work on the application of these procedures to the analysis of smokeless powders was discontinued because the chromatographic-spectrophotometric procedures described below were found to be thoroughly satisfactory.

Determination of Acardite. Acardite can be estimated quantitatively by the volumetric bromination procedure involving acetic acid. A chromatographic procedure for the estimation of this substance is described below.

Determination of Diphenylformamide. Diphenylformamide does not react with bromine at a significant rate under customary conditions of analysis. The results of experiments involving alkaline hydrolysis and estimation of the resulting diphenylamine were encouraging, but detailed analytical procedures were not developed because of the satisfactory nature of the chromatographic procedure described below.

Procedures for the Quantitative Estimation of Volatile and Inorganic Constituents

Determination of Moisture and Volatile Solvent. On the basis of existing specifications, four methods for the determination of moisture in solventless double-base powder (the desiccation, the cone-and-dish, the carbon tetrachloride distillation, and the Karl Fischer procedures) were selected and subjected to a critical investigation. The results are collected in a formal report.[154]

Desiccation over concentrated sulfuric acid was found to be the most reproducible procedure of those examined. Although at least four days is required for the determination of moisture by this procedure, the time of the analyst per analysis is less than that required for any of the other procedures. Additional experiments indicated that desiccation under these conditions removes virtually all of the moisture but not more than a few hundredths of a per cent of the other constituents present in a powder sample.

The cone-and-dish procedure[155] for the estimation of total volatile matter is rapid and gives reasonably satisfactory results for the analysis of solventless powders containing from 0.2 to 0.4% moisture; however, its success appears to be due to a balance between incomplete removal of water and loss of other constituents from the system.

Reflux distillation of the powder sample with carbon tetrachloride, and collection of the water in a calibrated trap is a satisfactory procedure for rapid control analyses in which an accuracy of 0.05% is satisfactory. Errors due to sampling are reduced because a 100-g sample of powder is required for this procedure.

Procedures involving the use of Karl Fischer reagent[156] are satisfactory when proper precautions are taken, but they cannot be recommended for control analyses.

No studies were made of any procedure except the cone-and-dish for the determination of volatile constituents other than moisture.

Determination of Nonvolatile Inorganic Constituents. New chemical, spectrographic, and polarographic procedures that have been developed for the identification and estimation of nonvolatile inorganic constituents in smokeless powder are described in a formal report;[157,158] the findings are summarized in the following paragraphs.

Routine chemical procedures may be employed for the semi-quantitative analysis of cationic and anionic constituents in smokeless powders. Most of these procedures are rather tedious and are not highly precise when applied to the estimation of constituents which are present only as traces. However, procedures for the estimation of moderate amounts of such constituents as graphite, carbon black, potassium nitrate, potassium sulfate, potassium perchlorate, and titanium dioxide have been shown to be satisfactory and are described in reference 157; procedures for the estimation of carbon black and potassium perchlorate in EJA powders are described in more detail in a formal report on a complete procedure for the analysis of these powders.

A rapid spectrographic procedure which has been developed for the semi-quantitative estimation of cationic constituents is a great improvement over the more cumbersome chemical procedures. The spectrograph has proved to be very valuable for the preliminary study of a powder of unknown composition and for the estimation of metals present only as traces.

Polarographic procedures have also proved to be helpful for the determination of chloride, nitrate, nitrite, titanium, barium, and alkali metals.

A simple conductometric method has been developed for the rapid approximate determination of the total percentage of water-soluble inorganic salts in a powder.

In addition to the various semi-quantitative procedures described above, X-ray diffraction studies have been found to be a valuable aid in the identification of crystalline constituents. These studies are especially helpful in the examination of mixtures because they

provide information concerning the combination of cations and anions in the original powder. Diffraction data have been obtained for magnesium, aluminum, ammonium nitrate, potassium nitrate, strontium nitrate, barium nitrate, potassium sulfate, barium sulfate, sodium chlorate, potassium chlorate, potassium perchlorate, and titanium dioxide (rutile).

6.11.2 Chromatographic-Spectrophotometric Methods[r]

In 1906 a new method for the separation of the constituents of a mixture by selective adsorption was developed by the Russian botanist Tswett. This method, which was based on the unidirectional flow of a solution of the mixture through a column of adsorbent, was especially adaptable to the separation of colored substances; it was therefore termed "chromatographic analysis" or, more simply, "chromatography." Although the potentialities of this new technique were recognized by a few investigators, little application of it was made prior to 1931. Since that year, however, the use of chromatography has become widespread, especially in the separation and purification of naturally occurring organic compounds; its application to inorganic substances has been limited.

When work on propellants was begun at the California Institute of Technology in the spring of 1942, the applicability of chromatography to the problems of powder chemistry was recognized at once, and a series of investigations was undertaken under OSRD Contract OEMsr-702. After July 1, 1943, this work was continued and extended under OSRD Contract OEMsr-881.

The chromatographic method has proved to be especially valuable in the study of explosives when it is combined with the technique of absorption spectrophotometry. By the use of chromatography it is possible to effect many separations and purifications which would be difficult or impossible to achieve without this technique; the compounds so isolated can, in most cases, be simply and accurately identified and estimated spectrophotometrically.

The following summary of the chromatographic and spectrophotometric investigations which were done,[s] includes a very brief general description of the chromatographic method, a discussion of the development of the chromatographic-spectrophotometric method and of its application to the study of smokeless powders and related substances, and a short discussion of certain phenomena and relations which were observed during these studies and which are of general applicability in chromatographic and spectrophotometric work.

The general methods of chromatography, the development of chromatographic-spectrophotometric techniques for application to the study of smokeless powders, the chromatographic properties and absorption spectra of all of the compounds studied, and procedures for the quantitative determination of all of the important constituents of powders have been described in detail in reports issued from the California Institute of Technology.[159-163]

A colored motion picture which illustrated the operations and techniques of chromatography has also been prepared.

The Chromatographic Method

The chromatographic method is best adapted to the isolation of compounds in quantities which are of the order of a few hundredths of a milligram to about fifty milligrams. The chromatographic process is carried out in a vertical glass tube which consists of two sections, a long cylinder and a special adapter by means of which the cylinder is mounted on a filter flask. The chromatographic column is formed, or "packed," by pouring the adsorbing material, the adsorbent, into the tube under the full force of an aspirator, by means of which a strong suction is maintained throughout the chromatographic experiment. The mixture to be analyzed is dissolved in a small volume of some selected solvent from which the substance will be strongly adsorbed. This solution is then poured upon the adsorbent and drawn by continuous suction into the column. Upon the subsequent addition of portions of the same solvent, or of a different solvent, or mixture of solvents, the adsorbed substances migrate slowly down the column at rates which depend upon their respective adsorption affinities. This procedure is termed *development,* and the solvent or mixture of solvents which is used to effect the separation of the adsorbed substances is called the *developer.* When development has been properly carried out the various solutes are distributed through the adsorbent in a series of well-defined zones, separated from each other by portions of the column which are free of adsorbed material. The most strongly adsorbed substance is nearest the top of the column, and the least strongly adsorbed nearest the bottom. When proper separation has been attained the development is halted and the column is extruded from the tube.

[r] This section is taken from a report submitted by Kenneth N. Trueblood.

[s] OSRD Contracts OEMsr-702 and OEMsr-881.

If some of the constituents of the mixture form colorless zones on the column, these zones may usually be located on the extruded chromatogram by applying thin streaks of suitable reagents along the entire length of the column; a suitable reagent for a particular substance is one which produces a noticeable color throughout a zone of the compound. The location of colorless zones for which a streak reagent cannot be found is a more difficult and tedious task and can usually only be done empirically; occasionally use can be made of some special property of a compound such as fluorescence in ultraviolet light.

After the zones have been located they are separated from each other by cutting the column into sections; all portions which are contaminated with streak reagent are carefully removed and discarded. The individual zones are then transferred to separate flasks and mixed with a suitable solvent which removes the adsorbed substance from the adsorbent; this process is termed *elution* and the solvent which is used is called the *eluent*. The suspended adsorbent is removed from the mixture by filtration through a sintered glass funnel, and elution is completed by drawing additional quantities of eluent through the filter cake. The filtrate thus obtained is termed the *eluate*. The process of elution is the final step in the chromatographic procedure.

The eluate of each of the separate zones contains, ideally, only one compound; sometimes, however, it is impossible to achieve a complete separation of all of the constituents of a mixture in one chromatogram. In such case certain of the zones will contain two or more compounds. Such mixtures can usually be separated by rechromatography; the eluate of the zone is freed of solvent by evaporation, and the residue is dissolved in a suitable solvent, and is again chromatographed, usually under slightly different conditions than before.

After each zone has been purified to the desired extent, the course of further investigation of the eluate will depend upon the nature of the substance or substances in the eluate and upon the objectives of the work. A discussion of some of the possible procedures is given here.

Development of the Chromatographic-Spectrophotometric Method for Application to the Study of Smokeless Powders and Related Substances

A considerable amount of preliminary experimentation was necessary before the methods of chromatography and spectrophotometry could be applied successfully to the analysis and study of smokeless powders and related substances. A brief account of the principal problems which arose and of the manner in which these problems were solved is presented in the following paragraphs; a detailed discussion is given in references 160 to 162.

The first and perhaps the most important task was the selection of a suitable chromatographic adsorbent. Some early success was achieved with calcium hydroxide, Neutral Filtrol, alumina, and talc; however, each of these adsorbents possessed certain undesirable characteristics. Silicic acid, on the other hand, appeared to be entirely satisfactory for the chromatography of the constituents of smokeless powder and was, therefore, used almost exclusively throughout the entire program of work; *the discussion which follows applies to chromatographic work on silicic acid unless specifically stated otherwise.* Because the rate of filtration of solvents through silicic acid is extremely slow it is desirable for chromatographic purposes to mix the silicic acid with a filter aid. A mixture of two parts by weight of Merck's reagent silicic acid with one part of Celite 535, a product of the Johns-Manville Corporation, is generally satisfactory as an adsorbent; minor variations from the 2/1 ratio are sometimes desirable because of variations in the rates of filtration through different lots of silicic acid.

Preliminary experiments on the chromatography of nitrocellulose met with no success; furthermore the presence of this material on the column during the chromatographic determination of the other constituents of powder proved to be very objectionable. Hence a procedure for the quantitative separation of the nitrocellulose from the other organic constituents which are present in a smokeless powder was necessary. Extraction of the powder in a Soxhlet apparatus has been used for this purpose by powder chemists, but an excessively long time is usually required for complete extraction. It was found, however, that the efficiency of the method can be greatly increased by first subdividing the powder into pieces about 0.1 mm thick; this can be done conveniently with a sliding microtome, using a special cutting tool for especially hard powders. A double-base powder can then be completely extracted with anhydrous ether or methylene chloride in two or three hours; a somewhat longer time is required for FNH or single-base Pyro powders. With the exception of inorganic material, nitrocellulose, and a few other substances which are extremely insoluble in the extracting agents, all the common constituents of powders will be present in the extract.

Because ether is an eluent for most substances, it must be removed entirely from an extract before chromatography, in order that the substances in the extract will be adsorbed and not merely washed through the column. The complete removal of the ether is satisfactorily accomplished by evaporation in a slow stream of air. The residue may then be dissolved in benzene, diluted with about an equal volume of ligroin, and chromatographed. A methylene chloride extract need not be evaporated; it may be chromatographed directly after dilution with about an equal volume of ligroin. Methylene chloride is at least as efficient as ether as an extracting agent for powder; indeed, some evidence indicates that it may even be superior.

In general a satisfactory solvent for placing a compound on a chromatographic column, is one which is a very weak developer for the compound; if the solvent is a strong developer or an eluent for the particular substance, the latter will be spread throughout most or all of the column and proper development will be impossible. Ligroin is essentially an ideal solvent for placing most substances on the chromatographic column because it has almost no developing action. If a compound is insoluble in ligroin it is generally possible to obtain a satisfactory solvent by dissolving the compound in a stronger developer and diluting the resulting solution with ligroin until the developing action is sufficiently weakened. Benzene is most frequently used with ligroin in this manner.

It must be emphasized that the term "developer" is a relative one; a mixture of solvents which is a good developer for one compound may be an eluent of a second substance or may leave a zone of some third substance at the top of the column. In general the nore polar a solvent, the stronger its developing action. Thus, ligroin is the weakest developer, benzene and methylene chloride are somewhat stronger, and ether, ethyl acetate, acetone, and ethanol are powerful developers or eluents for most substances. By judicious selection and admixture of these solvents, and of others in certain special cases, a wide range of developing actions may readily be achieved.

The most common and convenient eluents are ether, ethanol, and a mixture of equal volumes of acetone and ether. A solvent which is used as an eluting agent should have no properties which interfere with or complicate subsequent operations upon the eluate.

Most of the common constituents of smokeless powders are colorless; the chief exceptions are the nitration products of the stabilizers, and these compounds are normally present only in small amounts. The positions of the colored zones on a column may sometimes serve as convenient indicators of the approximate positions of the colorless zones. However, accurate location of most colorless zones can be conveniently accomplished only by means of a streak reaction with some appropriate reagent. It is desirable that the streak reagents which are employed react with a wide variety of compounds, so that the number of streaks necessary to locate all of the colorless zones on a particular column may be kept to a minimum. Many streak reagents were developed for the various types of compounds which are to be found in smokeless powders; the most useful of these are a solution of ceric sulfate or vanadium pentoxide in sulfuric acid, applicable to a wide variety of phenyl-substituted ureas, urethanes, and related compounds; a solution of diphenylamine in sulfuric acid, applicable chiefly to nitric esters and N-nitroso compounds; an aqueous solution of sodium hydroxide or potassium hydroxide, a satisfactory reagent for many nitro compounds; and a solution of sodium nitrite in sulfuric acid, which gives colors with diphenylamine and certain of its derivatives. Several other streak reagents were found to be applicable to a limited number of compounds.

An ultraviolet spectrophotometer affords the simplest and most generally applicable means for the preliminary identification of unknown substances and the quantitative estimation of known compounds. With the aid of this instrument it is possible to identify as little as a few hundredths of a milligram of many compounds and to measure accurately quantities of the order of one milligram. Hence an ultraviolet spectrophotometer is almost indispensable for use in conjunction with the technique of chromatography.

In preliminary experiments on the quantitative recovery of certain constituents of smokeless powders from the chromatographic column, it was discovered that impurities in the adsorbent and in the various organic solvents used in the procedures made it impossible to obtain reproducible results. It was found that the solvents could be rendered sufficiently pure by distillation in an all-glass still; this method of purification was used thereafter for all solvents. The removal of the impurities in the adsorbent could be accomplished satisfactorily by washing the column with a specified volume of anhydrous ether and then with ligroin before introducing the sample. This "prewashing" treatment tends to make the adsorbent somewhat stronger by removing water from it; it was found later that a modified prewash employing a

mixture of equal volumes of acetone and ether increases the strength of the adsorbent even more by removing additional water. The prewashing treatment first described was used in most of the chromatographic work and was generally satisfactory; the modified procedure was employed only in special cases when the ordinary procedure was inadequate.

The most suitable solvent for spectrophotometric measurements is absolute ethanol. Many of the solvents which are commonly used as developers show appreciable absorption in the ultraviolet region of the spectrum, and, hence, interfere with a spectrophotometric measurement. Since an extruded column is usually still wet with an appreciable quantity of the developer some of this solvent will be carried, with the adsorbed substance, into the eluate and will thereby render impossible spectrophotometric measurements on the eluate. The objectionable solvent can readily be eliminated, however, by evaporation to dryness under reduced pressure. The absorption spectrum of the residue can then be measured after the material has been dissolved in absolute ethanol.

If the adsorbed compound is appreciably volatile it will be partially or completely lost when the eluate is evaporated to dryness. Hence, with such a compound an alternative method of removing the developer is to be preferred: after development has been completed, the chromatogram is washed with 28 to 38 C ligroin in order to remove the less volatile solvents, the zone is cut in the usual fashion, allowed to dry in air for about one hour, and then eluted directly with ethanol.

Certain modifications in the procedure outlined above are necessary in quantitative work. Calibrated glassware must be employed in diluting the extract of the powder, and in measuring the sample for chromatography, and special care must be taken to insure that the sample is transferred quantitatively to the column. In a quantitative determination the streak reagent is used only to delimit the zone and is not applied to the main portion; thus the losses because of contamination by streak reagent are minimized.

Before a compound can be quantitatively estimated with the aid of the spectrophotometer it is necessary that an extinction coefficient at a suitable wavelength be accurately measured with a pure sample of the substance. The most convenient wavelength is generally one at which the absorption spectrum of the compound has a maximum.

In all quantitative spectrophotometric work it is essential that calibrated glassware be used and that the temperature be controlled, because the *optical density* of a solution of a given compound varies directly with concentration. In addition it is necessary to make a blank correction for the entire chromatographic procedure and certain minor corrections incident to the method of measurement of the optical density.

Quantitative measurements can be made without the aid of a spectrophotometer, but they are considerably less convenient. For example, it is possible to isolate PETN by chromatography and to determine the quantity by direct weighing or to isolate nitroglycerin by chromatography and to determine the quantity by the usual volumetric procedure. In general, however, spectrophotometric estimation is much to be preferred when it is feasible; nitric esters are among the few constituents of smokeless powders which cannot conveniently be estimated spectrophotometrically.

Applications of the Chromatographic-Spectrophotometric Method to the Study of Smokeless Powders and Related Substances

The chromatographic-spectrophotometric method can be applied successfully to a variety of analytical problems in powder chemistry; the applications which have already been made range from routine quantitative estimation of the common constituents of powders to exhaustive qualitative and quantitative analyses of powders of unknown composition. The exact manner in which a particular problem should be attacked cannot of course be specified, but the following generalizations can safely be made.

If the components of the mixture to be analyzed are already known, as, for example, in the analysis of an American propellant, it is generally necessary only to experiment with pure samples of these compounds until an effective scheme for the quantitative separation and estimation of the desired material has been devised. In the analysis of a powder of uncertain composition, such as a foreign propellant or an artificially aged powder, a complete qualitative analysis must first be made. Even when all the components of a powder are not known it is sometimes possible to predict what compounds are likely to be present; a preliminary study of the properties of these substances will then greatly simplify their detection and estimation in the powder. Frequently, however, completely unfamiliar compounds are detected; the general manner in which the identification of such substances is effected can be outlined briefly as follows.

The chromatographic behavior, streak reactions, and absorption spectrum of an unkown compound are first

compared with those of all of the known compounds which have been investigated. This procedure often affords important clues as to the nature of the unidentified material; for, after a sufficient number of compounds have been examined, certain correlations can often be established between the structure of a compound and its streak reactions, chromatographic behavior, and absorption spectrum. Sometimes an unknown compound may be isolated in sufficient quantity and purity for melting-point determination, microanalysis, or other appropriate treatment.

If the readily available evidence as to the identity of the unknown is insufficient for positive identification, the only remaining course is to prepare or obtain the compounds which have the most likely structures and to compare the properties of these compounds with those of the unknown material. Hence, a complete qualitative analysis is often a long, laborious task.

During the course of the studies of smokeless powders and other explosives by chromatographic and spectrophotometric methods, detailed investigations were made of the chromatographic behavior of a wide variety of compounds. The characterization of the chromatographic behavior of a compound involves the determination of a suitable solvent for placing it on the column, of a means for locating it on the column, of its behavior with several different types of developers, of methods by which it may be separated from other compounds of similar adsorption affinity, and of a satisfactory eluent. More than thirty explosives, stabilizers, and plasticizers were investigated, including all of the common constituents of single-base and double-base powders, with the exception of nitrocellulose and inorganic substances. A detailed and complete investigation was made of the chromatographic behavior of RDX, and of nine of the compounds closely related to it in connection with the development of a method for the analysis of commercial samples of RDX for impurities (see Section 1.2). Extensive investigations of the transformations of diphenylamine and centralite in their roles as stabilizers in smokeless powders required a thorough study of the chromatographic properties of about twenty nitration and nitrosation products of diphenylamine and about twenty-five compounds which are related to ethyl centralite. The derivatives of diphenylamine were chromatographed on calcium hydroxide as well as on silicic acid; the former adsorbent was, however, preferable only for a few specialized separations.

The absorption spectra of all the above-mentioned compounds, and of about fifty others related to them, were measured in absolute ethanol with a Beckman ultraviolet spectrophotometer. The related compounds included some substances which were considered as possible transformation products of diphenylamine or centralite but which were never detected in powders, some compounds which were prepared for testing as stabilizers and plasticizers in experimental powders, and a few miscellaneous compounds.

Chromatographic - spectrophotometric procedures were developed for the quantitative estimation of almost all the stabilizers and plasticizers and a few of the explosives which were encountered in American and foreign propellants. Most of these procedures were simpler and more general in applicability than the older and more conventional chemical methods; for several of the compounds no analytical procedure other than the chromatographic-spectrophotometric one has yet been developed. Methods were also devised for the roughly quantitative estimation of many of the transformation products of diphenylamine and centralite in powders.

Although the quantitative and roughly quantitative procedures could be standardized to some extent, frequent checking and occasional modification or revision were essential because of the possible presence in a powder of previously unencountered compounds and because of variations in the adsorptive strength of the silicic acid from lot to lot.

Routine Analyses. One of the commonest, though least exciting, applications of chromatographic-spectrophotometric techniques has been in routine quantitative analyses for certain common constituents of various standard powders.

Precise and reliable methods have been developed which are in most cases equal or superior to older methods both in convenience and accuracy. Although it is not possible to determine nitric esters spectrophotometrically, the chromatographic method is of great advantage in the analysis of mixtures of these substances which are otherwise difficult to analyze. For example, a mixture of nitroglycerin and diethylene glycol dinitrate can be separated quantitatively into its components by chromatography, and the individual esters can then be separately estimated by the standard volumetric procedures.

Analyses of Foreign Propellants. The chromatographic-spectrophotometric method is best adapted for use with micro or semi-micro quantities of material, and for this reason it is ideally suited to the

analysis of small samples of smokeless powder of unknown composition. A typical qualitative analysis requires perhaps 0.5 g of powder and a quantitative analysis can usually be completed with less than 2 g. The identification of a hitherto unencountered component of a powder is greatly simplified by a study of its absorption spectrum and chromatographic behavior, particularly in regard to its streak reactions. If necessary, a few centrigrams of the material can readily be isolated for microanalysis.

Examples of the application of the chromatographic-spectrophotometric method to the analysis of foreign propellants are included in several reports[106,107] and are discussed in Section 6.14.

Investigations of the Chemical Changes Which Take Place in Smokeless Powders under Various Conditions. The chromatographic-spectrophotemetric method is the only satisfactory technique yet developed for studying the complex chemical reactions which take place in smokeless powder under various conditions, such as aging, irradiation, and storage at elevated temperatures. The method has so far been applied exclusively to the study of the transformations of the stabilizers, in particular, diphenylamine and centralite: the investigation of the degradation products of the explosive constituents of a powder would be an extremely complex task, especially since the spectrophotometer would be of little use.

An early attempt to study the effects of irradiation on several double-base propellants by spectrophotometric examination of thin sections of these powders met with little success.[164,165] Although a fairly satisfactory method for measuring the absorption coefficients of the powders was devised, lack of information as to the nature of the absorbing compounds prevented a complete appraisal of the effects of the irradiation.

One of the early applications of chromatographic-spectrophotometric techniques was in a study of the effect on the diphenylamine content of ballistite of the processing operations which are incident to the preparation of this powder for use in rocket motors.[166] It was found that the percentage of stabilizer in the powder decreased negligibly during these operations.

A variety of techniques was used to investigate the stability of propellants, as discussed in Section 6.12; one of these methods was the study of the rate of depletion of the stabilizer during storage at elevated temperatures. It was hoped that a comparison of the rates of depletion of a given stabilizer in powders of similar but slightly different composition, would indicate the effects of certain variations in composition on the relative stabilities of the powders. Among the powders which were studied after storage at temperatures near 70 C (about 160 F) were trench mortar sheet,[167] a series of modified ballistites,[168,169] several double-base powders which contained RDX but no nitroglycerin,[96] and two Albanite powders (see Section 6.7). In addition, a study was made of the rate of depletion of diphenylamine in ballistite JP 204 and in an FNH powder, RPL 141, at 80, 90, 100, and 110 C in the vacuum stability test.[170] The results of all of these studies are discussed briefly in Section 6.12.

An exhaustive study was made of the transformation products of diphenylamine in double-base powders,[171] and in FNH and single-base pyro powders,[120] during storage at elevated temperatures. With the exception of a compound which contained the cation of diphenylamine blue, a triphenylmethane-type pigment which was detected in small amount, all the identified products from both types of powders were nitro and N-nitroso derivatives of diphenylamine. The derivatives which were found in double-base powder may be listed as follows:

N-Nitrosodiphenylamine
2-Nitrodiphenylamine
4-Nitrodiphenylamine
N-nitroso-2-nitrodiphenylamine
N-nitroso-4-nitrodiphenylamine
2,2′-Dinitrodiphenylamine
2,4-Dinitrodiphenylamine
2,4′-Dinitrodiphenylamine
4,4′-Dinitrodiphenylamine
N-Nitroso-2,4′-dinitrodiphenylamine
N-Nitroso-4,4′-dinitrodiphenylamine
2,2′,4-Trinitrodiphenylamine
2,4,4′-Trinitrodiphenylamine
2,2′,4,4′-Tetranitrodiphenylamine
2,2′,4,4′,6-Pentanitrodiphenylamine
2,2′,4,4′,6,6′-Hexanitrodiphenylamine
2,4,6-Trinitrophenol (picric acid)

According to the results of quantitative determinations of diphenylamine and its derivatives in a series of samples of ballistite JP 204 which had been stored at 71 C, the first reaction of diphenylamine is apparently an overwhelming conversion to N-nitrosodiphenylamine. After the diphenylamine has been exhausted, N-nitrosodiphenylamine decreases rapidly, and N-nitroso-4-nitrodiphenylamine and the dinitro and trinitro derivatives make their appearance. Tetranitrodiphenylamine appears when the trinitro compounds are present in considerable quantity and increases rapidly when most of the material is in the form of the trinitro derivatives. When the tetranitro derivative is present in large quantity, pentanitrodiphenylamine, hexanitrodiphenylamine, and some picric acid are produced.

In FNH and a single-base pyro powder, the transformation of diphenylamine had only reached the

stage of the trinitro derivatives in the last samples which were studied; however, up to this point the course of the transformation resembled closely that which was found to take place in double-base powder.

The actual reactions involved in the consecutive transformations of diphenylamine into its derivatives are not yet known. There is definite indication that, in addition to a scheme of nitrosamine rearrangement as in the Fischer-Hepp reaction, followed by oxidation, many other types of reactions are responsible for the transformations. These possible reactions include N-nitrosation, denitrosation, direct nitration of amines or nitrosamines, and the oxidation of nitrosamines to nitramines followed by rearrangement. Studies of several experimental double-base powders in which diphenylamine derivatives were incorporated showed that N-nitrosation and denitrosation are important in certain stages of the degradation of the stabilizer.

By assuming that the reactions responsible for the consecutive transformations of diphenylamine occur by a simple scheme and that the reactions are pseudo first order, reaction rate constants for the formation and destruction of each derivative in double-base powder have been determined. No corresponding analysis has been performed for the reactions in single-base powder.

An outstanding difference between ballistite and single-base and FNH powders lies in the overall rate of transformation of diphenylamine and its derivatives. The rate of transformation in single-base pyro powder is only one-tenth that in ballistite; in FNH powder, transformation proceeds at an even slightly slower rate. In double-base powders which contain RDX in place of nitroglycerin, the rate of depletion of diphenylamine is comparable to that in single-base powder and is much smaller than that in ballistite.

After the exhaustion of diphenylamine the percentage of diphenylamine which is accounted for as its derivatives falls to a nearly constant level, 60 to 65 per cent, in single-base as well as in double-base powder. In FNH powder, on the other hand, the recovery of diphenylamine is substantially 100 per cent until the diphenylamine is exhausted and is comparatively high thereafter. It is not known why the addition of dinitrotoluene to pyro powder or its substitution for nitroglycerin in ballistite should inhibit the reactions which are responsible for the loss of diphenylamine.

A careful study of the transformation products of ethyl centralite in double-base powders during storage at about 70 C was likewise made.[119] Both cordite JP 76, which contains 9% of centralite, and Radford Pilot Lot No. 142, which contains 1% of this stabilizer, were investigated. These studies proved to be considerably more complex than the investigations of the transformation of diphenylamine; the transformation of centralite takes place more slowly, and the course of the reactions is less clear than with diphenylamine.

The identified transformation products of centralite may be classified in two general groups. One group contains the compounds in which the urea structure is still present, and the other those in which it has been split. The chief compounds so far detected in the first category are 4-nitrocentralite, 4,4′-dinitrocentralite, and 2,4,4′-trinitrocentralite; the latter compound has been found only in small amounts in the longest-heated samples. 2-Nitrocentralite and N-ethylcarbanilide are also found but are present in much smaller amount than the other compounds. In the second category the chief products are N-nitroso-N-ethylaniline and N-nitroso-4-nitro-N-ethylaniline; traces of other compounds such as 4-nitro-N-ethylaniline, 2-nitro-N-ethylaniline, 4-nitroaniline, and 4-nitrophenol can also be detected. In addition to the compounds which have been identified, there are several apparently minor unidentified substances whose streak reactions and adsorption spectra resemble those of some of the known derivatives. To aid in the study of the course of the transformations of the derivatives of centralite, several experimental powders which contained various transformation products of centralite as stabilizers were prepared.

At 65 C the transformation of centralite in cordite JP 76 differs notably from that in RPL 142. In cordite N-nitroso-N-ethylaniline is the major primary transformation product of centralite, although some 4-nitrocentralite is also formed; in RPL 142, on the other hand, the situation is reversed and 4-nitrocentralite predominates. Furthermore the rate at which centralite disappears from cordite is about five times as great as that at which it is depleted from RPL 142. In each powder, after depletion of the centralite, only about one-half of the centralite which has disappeared can be accounted for in terms of known derivatives. It has been determined that no more than a minor portion of the "missing" centralite is volatilized during the heating of the powders.

It is apparent that a considerable amount of work on the transformations of centralite in double-base powder remains to be done. In this connection it

should be mentioned that a parallel investigation of the applications of chromatography to the examination of explosives and, in particular, of heated cordite is in progress in England.[172-176]

Analysis of Commercial RDX. Chromatographic-spectrophotometric techniques were successfully applied to the analysis of commercial production lots of RDX and RDX(B),[177,178] These experiments have been described in Section 1.2.

Concluding Remarks

During the chromatographic studies of smokeless powders and related substances, many phenomena and relations were observed which are of interest and value in the general application and theory of chromatography. Because these matters were not of primary concern, however, the observations pertaining to them were usually only incidental.

First, the relative chromatographic positions of many similar compounds were considered, and some observations were made on the relation between the structure of a compound and its adsorption affinity on silicic acid. It was soon noted that the adsorption affinity of one compound relative to another is often a function of the type of developer which is employed; frequently it is possible to produce an inversion in the positions of two substances by a change in the type of developer. Later it was discovered that the position of one compound relative to another can often be changed merely by an alteration in the developing strength of a developer without any change in the nature of the components of the developer; this appears to be related to a phenomenon which has been termed the "threshold effect." Finally, a number of instances were found in which a presumably homogeneous compound produced two distinct and separate zones on the chromatographic column under certain specified conditions. Although some examples of this anomalous "double zone effect" could apparently be explained in various ways, others defied all interpretation.

6.12 STABILITY OF PROPELLANTS[t]

Studies of the stability of propellants by Division 8 divide themselves into two parts: studies of double-base powders at the California Institute of Technology and studies of other propellants at the Explosives Research Laboratory. There was so little overlapping of these two programs that they are best discussed separately. We shall begin with the work of the Explosives Research Laboratory.

Surveillance studies over a period of two and a half years showed that solvent-extruded composite propellants (Section 6.2) and powders related to Albanite (Section 6.7) had more than adequate stability for military purposes. It was shown further that the results of the 65 C surveillance corresponded well with practical observation of powder stability. Analyses of the stabilizer content of samples under surveillance gave useful estimates of the life of the powder. By contrast, the 120 C and the 135 C thermal stability tests and the Bergmann-Junk tests were of little usefulness.[70,179]

A theoretical treatment has been made of adiabatic ignition. The theory predicts the rate of self-heating of an explosive for which kinetic constants on decomposition are available. Since the rate constant and activation energies were available from gas evolution measurements for NENO and MNO, it was possible to calculate the ignition times of these explosives under adiabatic conditions; the calculated and experimental results agreed well. The theory accurately predicted the entire time-temperature curves for the self-heating of these explosives.

The test was then applied to solvent-extruded composite propellants, and to powders which contain stabilizer. (Unless stabilizer is present the decomposition is autocatalytic, and the equations for adiabatic ignition do not apply.) In the absence of autocatalysis a powder cannot decompose faster than it will under strictly adiabatic conditions. The results of adiabatic ignition experiments, therefore, permit a calculation of the minimum life of a powder under any conditions, provided only that stabilizer is present.

The program of studies of the stability of smokeless powder at the California Institute of Technology included the development and extensive application of chromatographic - spectrophotometric techniques for the measurement of the amount of stabilizer and of the transformation products of stabilizers in double-base powder, the development of a technique for the application of the vacuum stability test to the examination of small samples of double-base powder, the development of a highly modified form of the Taliani-type test, and the development of a standard procedure for making pH measurements on double-base powders. In addition, preliminary experiments

[t]The discussion of the stability program at the California Institute of Technology is taken from a summary prepared by Jerry Donohue, William N. Lipscomb, John W. Otvos, and David P. Shoemaker.

were made leading to the development of other stability tests: a test based on the interaction of powder and nitrogen dioxide at room temperature, a rocket safe test, and a test for "available nitrite" in double-base powder.

One result of this program was the accumulation of a large quantity of new data relating to the stability of single-base and double-base powders having a wide variety of compositions. For example, vacuum stability tests were made on over 500 powders of which over 200 were pilot lots[180] of rocket propellants which were submitted by the Army and Navy. Other investigations showed that there was no correlation between the stability and the color changes undergone by a certain powder, and that powder made from 100% rework was as stable as that made without reworked material.[181,182]

The results of all these stability tests are summarized briefly in the following ten subsections.

6.12.1 Consecutive Transformation of Diphenylamine in Double-Base Powder

A systematic investigation of the consecutive transformation of diphenylamine in double-base powder upon storage at surveillance temperatures was carried out using the chromatographic-spectrophotometric analytical techniques described in Section 6.11. The results of this study, and an extended discussion of them have been presented in a formal report[120] dealing with the stabilization of smokeless powder by diphenylamine; they are briefly summarized in the following paragraphs.

Samples of JP 204, a ballistite stabilized with diphenylamine, were stored at 71 C for various periods of time up to over 174 days. As the samples were removed from storage, analyses were made for diphenylamine and all of its nitro and nitroso derivatives which had been previously detected in artificially aged ballistite. These analyses accounted for only 50 to 60 per cent of the original diphenylamine content of the powder; the fate of the remaining diphenylamine is not known. The heating also resulted in the formation of dark-colored pigments, at least one of which was shown to be related to diphenylamine blue. The analytical data which were obtained by chromatographic-spectrophotometric methods are shown in Table 7.

A schematic representation of reactions which might be involved in the consecutive transformation of nitroso and nitro derivatives of diphenylamine is shown in Figure 10.

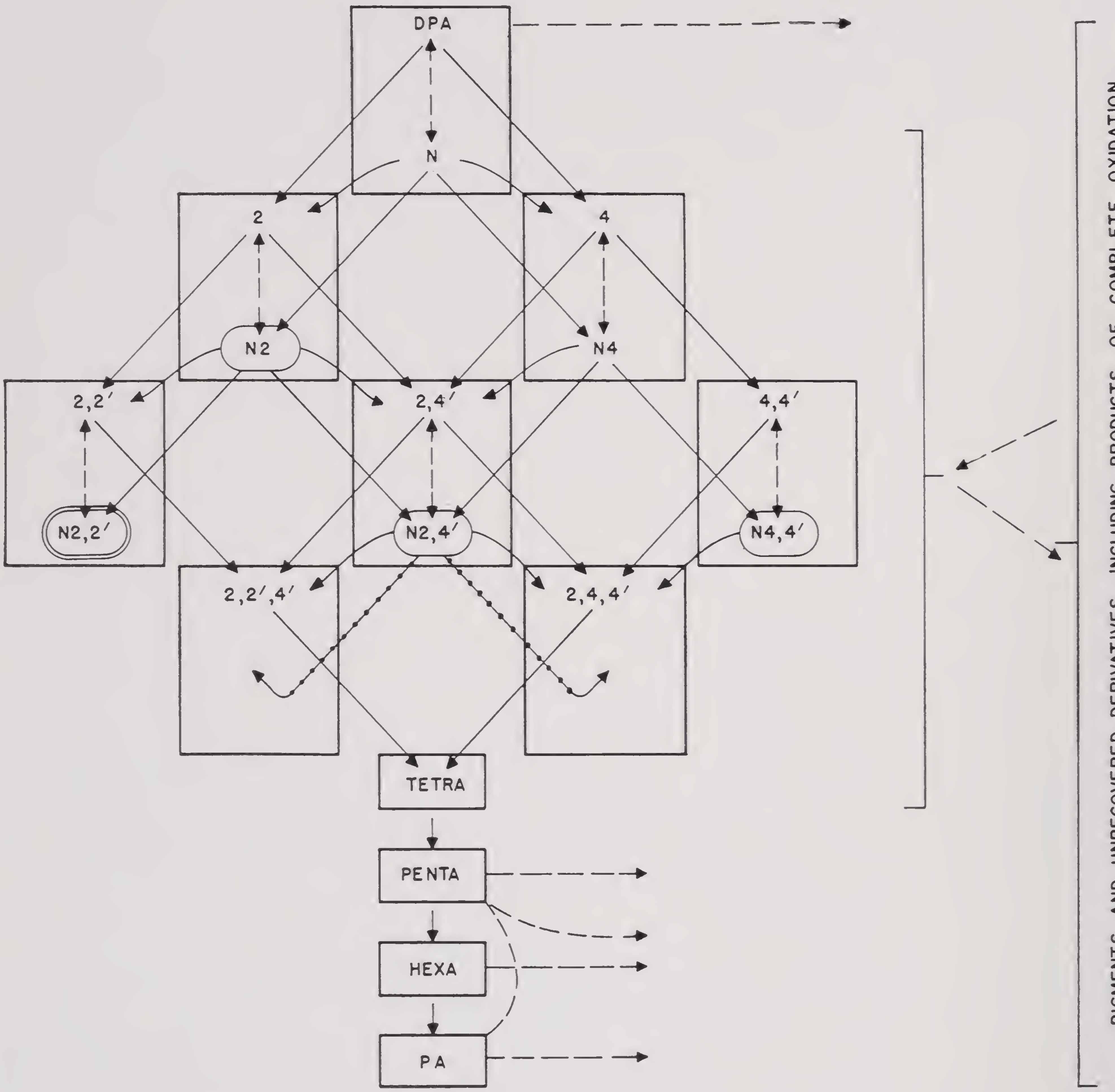
A mathematical treatment of the reactions involved in the consecutive transformations of diphenylamine was carried out on the assumption that they constituted a system of pseudo first-order reactions.[u] For the details of the mathematical analysis, see refer-

[u]A system of pseudo first-order reactions may be defined as one in which a set of consecutive and competing reactions which do not follow the first-order law may nevertheless be amenable to the mathematical treatment for first-order reactions provided the effective first order rate constants, although themselves not constant, have constant ratios to each other.

TABLE 7. Derivatives of diphenylamine isolated from grains of ballistite JP 204 during storage at 71 C.*

	Duration of heating (days)												
	0	2	4	8	20	35	48	82	124	174		258	
										Yellow	Red	Yellow	Red
Content of:													
Diphenylamine	7.11	4.27	1.60	0.0	†								
N-NO-DPA	0.42	2.08	3.55	4.47	2.35	0.78	0.18	0.01					
2-NO_2-DPA	0.08	0.13	0.10	0.31	0.24	0.09							
4-NO_2-DPA	0.02	0.07	0.09	0.14	0.35	0.18	0.04						
N-NO-4-NO_2-DPA	....	....	....	0.45	0.96	0.21							
2,2′-diNO_2-DPA	....	....	....	0.04	0.29	0.45	0.42	0.04					
2,4′-diNO_2-DPA	....	....	....	0.19	1.01	1.51	0.95						
4,4′-diNO_2-DPA	....	....	....	0.06	0.56	0.83	0.47						
2,2′,4-triNO_2-DPA	....	....	....	0.02	0.16	0.67	1.36	2.08	1.84	0.06			
2,4,4′-triNO_2-DPA	....	....	....	0.01	0.34	1.57	3.21	2.18	0.01				
TetraNO_2-DPA	....	....	....	....	....	0.07	0.23	3.51	7.52	2.75	0.57	0.31	0.45
PentaNO_2-DPA	....	....	....	....	....	....	....	....	0.09	2.40	0.75	0.91	0.80
HexaNO_2-DPA	....	....	....	....	....	....	....	....	....	4.75	6.25	6.13	5.96
Picric acid	....	....	....	....	....	....	....	....	....	0.16	0.0	0.18	0.25
Wt DPA equiv to sum of cpds	7.55	6.24	4.79	4.68	4.65	4.12	4.03	4.10	4.70	4.37	3.01	3.04	3.05

*Results are expressed in milligrams of each compound isolated from one gram of powder.
†Where no value is given the quantity is less than 0.01 mg.



DPA	- DIPHENYLAMINE
N	- N-NITROSO-DPA
2	- 2-NITRO-DPA
4	- 4-NITRO-DPA
N2	- N-NITROSO-2-NITRO-DPA, ETC
TETRA	- 2,2′,4,4′-TETRANITRO-DPA
PENTA	- 2,2′,4,4′,6-PENTANITRO-DPA
HEXA	- 2,2′,4,4′,6,6′-HEXANITRO-DPA
PA	- PICRIC ACID

DIRECT NITRATION
N-NITROSATION AND DENITROSATION
REARRANGEMENT AND OXIDATION OR OXIDATION AND REARRANGEMENT
NITRATION ACCOMPANIED BY DENITROSATION
OTHER REACTIONS
ISOLATED FROM JP 204 SHEET, BUT NOT FROM GRAIN
NOT YET ISOLATED FROM ANY POWDER

FIGURE 10. Possible relations among diphenylamine derivatives.

[redacted]

ence 120. The procedure for evaluating the rate constants involved the assumption of a set of constants, the calculation of the resulting expressions for the concentrations of the various diphenylamine derivatives, a comparison of the corresponding curves with the experimental data, and the estimation of the corrections necessary to improve the agreement between the theoretical curves and the experimental points. This procedure was repeated until satisfactory agreement was obtained. A comparison of the theoretical curves thus obtained and the experimental points is presented in Figures 11 and 12. From the results of this treatment it was possible to obtain information relating to the relative reactivities in the powder of the substances responsible for the nitrosation and nitration of the stabilizer.

In addition to these studies on JP 204, a series of studies was made on powders in which various derivatives of diphenylamine had been incorporated as stabilizers. These powders were stored at 71 C, and chromatographic-spectrophotometric analysis were made to determine the apparent unimolecular rate constant for the disappearance of the stabilizer. By comparison of these rate constants with those obtained from the corresponding compounds in JP 204 it was possible to make an estimate of the relative concentration of nitrating agent involved in reactions with these various stabilizers.

These investigations have tremendously increased our knowledge of the fate of the stabilizer in a ballistite or similar powder. However, even these extensive analytical data do not necessarily provide a decisive answer to questions concerning the absolute stability of a powder or the relative merits of different stabilizing compounds. In most cases there is no way of interpreting them in terms of the important changes which take place in the explosive constituents of the powder. Nevertheless, in powders of comparable composition containing initially the same concentration of a given stabilizer, a comparison of the rates of consecutive transformation of the stabilizer may yield valuable information. The presence of an undesirable constituent which promoted the decomposition of the nitric esters might be indicated by the more rapid rate of transformation of the stabilizer in one powder than in another containing the same initial percentage of the same stabilizer.

Rather extensive discussions of the problems involved in the determination and comparison of the stabilities of powders are given in two formal reports.[120,183]

6.12.2 Studies of Stabilizer Depletion in Heated Powders

Many experimental studies involving the depletion of the stabilizer in powders during accelerated aging at elevated temperatures, were made with the use of chromatographic - spectrophotometric techniques.

In one of these series of experiments, samples of ballistite JP 204 were stored at various temperatures (80, 90, 100, and 110 C), and samples were removed after various times for chromatographic-spectrophotometric determinations of the content of stabilizer and several of its immediate transformation products. These data were obtained in order to supplement the experimental results of the investigations described in the preceding section. A similar series of experimental studies were made on an FNH powder, Radford Pilot Lot No. 141, which had been stored at 90 and 100 C. Simple mathematical treatments, similar to those discussed above have been carried out for these initial reactions in the transformation of diphenylamine.[170] The postulates on which this mathematical treatment was based are (1) that the reaction by which diphenylamine is consumed when smokeless powder is heated is first order with respect to diphenylamine, and (2) that the diphenylamine is consumed by a nitrating-nitrosating agent, the exact nature of which is unknown but whose concentration varies linearly with the time of heating, according to the equation $C = a + bt$, where a and b are constants and t is the time of heating. Although this treatment could be considered to have only approximate validity, it was possible to choose the constants in the resulting equations so that the agreement between calculated values and the experimental points was satisfactory. The results of this treatment suggested that the reaction by which diphenylamine is consumed in ballistite JP 204 differs only in rate from that in FNH powder RPL 141. From the results of tests on a series of powders containing varying percentages of diphenylamine it seems likely that diphenylamine is capable of direct reaction with one or more of the constituents of smokeless powder, at least in the range of temperature at which the tests were carried out.

A simplified mathematical analysis[184] was also applied to the initial reactions of a typical centralite-stabilized powder, Radford Pilot Lot No. 142, which had been heated for various lengths of time at 65, 75, and 110 C. The assumptions on which this treatment was based are that the reactions by which 4-

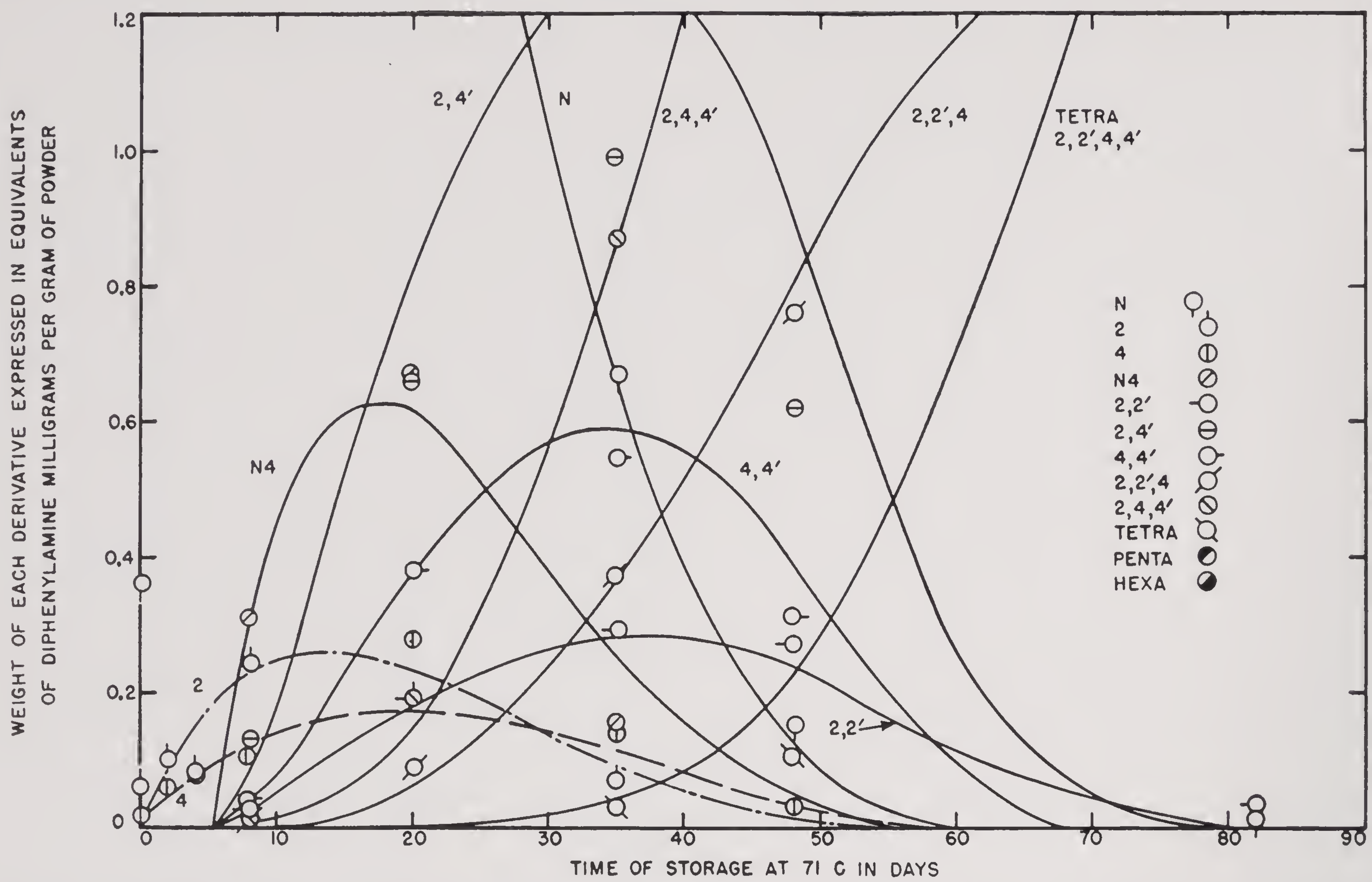


Figure 11. Transformation of diphenylamine in grains of ballistite JP 204 stored at 71 C. Comparison of theroretical curves with experimental data.

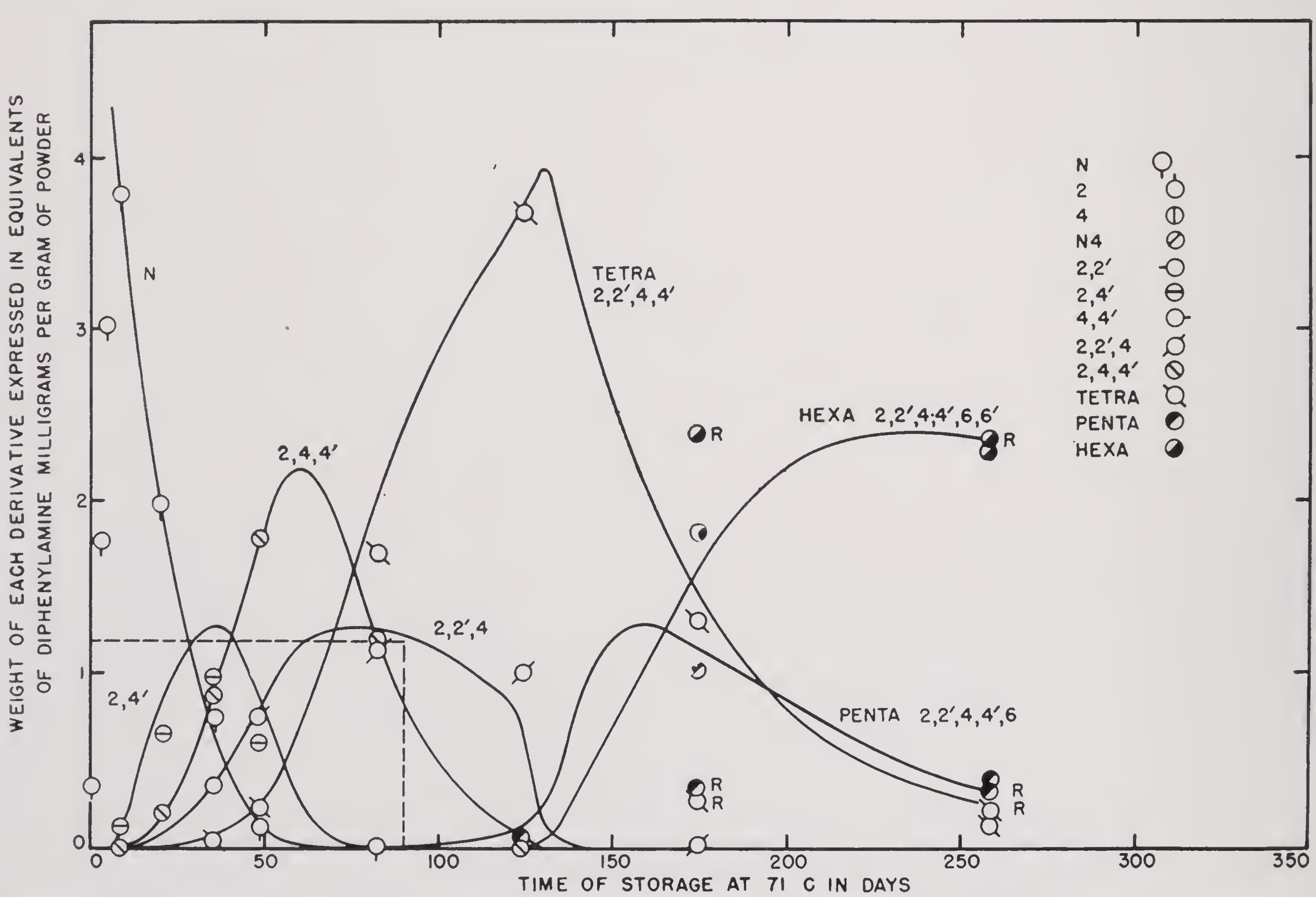


Figure 12. Transformation of diphenylamine in grains of ballistite JP 204 stored at 71 C. Comparison of theoretical curves with experimental data. R denotes red samples; the other samples were yellow.

nitrocentralite and N-nitroso-N-ethylaniline are formed from centralite, are first order with respect to centralite and that the depletion of 4-nitrocentralite is first order with respect to its concentration. It was possible to choose the constants in the resulting equations to give theoretical curves which gave satisfactory agreement with the experimental points as determined by chromatographic-spectrophotometric analyses of the samples. The results also indicated that at lower temperatures a smaller fraction of the centralite was converted to 4-nitrocentralite than at higher temperatures.

6.12.3 The Vacuum Stability Test

The vacuum stability test for explosives, which was devised by Farmer,[185,186] depends upon the fact that many explosives (particularly those which are nitric esters) slowly decompose, evolving gases, when they are heated in evacuated containers at elevated temperatures. The extension of this test to investigations of smokeless powders was carried out with the use of apparatus patterned after that of McGill.[187]

The experimental procedures and the results of these tests have been presented in several formal OSRD reports.[35,188-194]

In the vacuum stability test the powder sample (0.1 to 0.5 g) is heated in the sample tube of the apparatus shown in Figure 13, and the volumes (at STP) of the gas evolved after various times of heating are calculated from readings of the pressure which are made on the attached capillary manometer; the latter is maintained at room temperature. Most of the tests were made at 110 C; additional tests were also run at temperatures ranging from 80 to 120 C in order to provide a basis for extrapolation of the results to lower temperatures.

The results of the vacuum stability tests indicated that lower average rates of gas evolution are shown by the following powders.

1. Powders containing carbazole, β-nerolin, ethyl centralite, or nitro derivatives of diphenylamine, as compared with those containing diphenylamine.
2. Powders containing lower percentages of ethyl centralite or diphenylamine, as compared with those containing a higher percentage of either of these compounds.
3. Powders containing ethylphenylurethane or diphenylurethane, as compared with those containing comparable percentages of acardite.
4. Powders containing nigrosine, as compared with those containing carbon black or no darkening agent.
5. Double-base powders containing dinitrotoluene, as compared with those containing approximately the same percentage of trinitrotoluene.
6. Powders containing a higher ratio of nitrocellulose to nitroglycerin, as compared with those having a lower ratio.
7. Powders containing diethyleneglycol dinitrate in place of a comparable percentage of nitroglycerin.

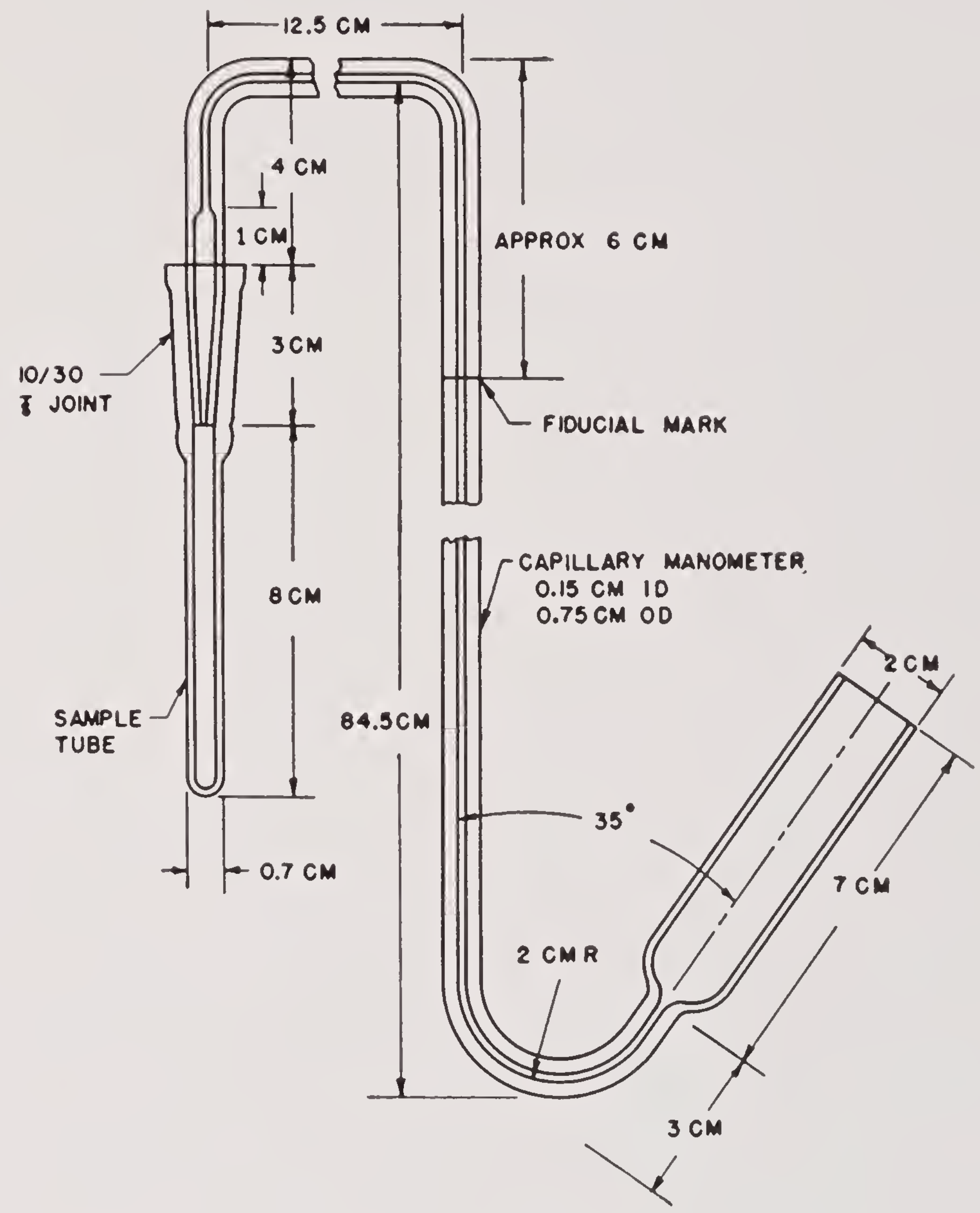


FIGURE 13. Standard-taper units for vacuum stability tests.

8. Powders containing a large percentage of potassium perchlorate (EJ powders), as compared with standard double-base powders.
9. Double-base powders containing RDX, Fivonite or DINA, as compared with those containing corresponding percentages of nitroglycerin.
10. Pyro or FNH single-base powders, as compared with standard double-base powders.
11. Standard double-base powders, as compared with those containing manganese dioxide.
12. Powders containing potassium sulfate or no salt, as compared with those containing potassium nitrate. (This difference is especially great.)
13. Powders containing no salt, as compared with those containing potassium sulfate or sodium chloride. (These differences are small.)

14. Powders containing alkaline earth nitrates as compared with those containing alkali nitrates.

The rate of gas evolution appears to be unaffected by the addition of small percentages (0.1%) of lead stearate or candelilla wax.

The addition of small quantities of inorganic salts to double-base powder was found to increase its rate of gas evolution: potassium nitrate promoted gas evolution more strongly than almost any other salt examined; potassium sulfate ordinarily had little or no effect. The magnitude of the effect depended to a considerable extent on the nature of the particular salt added, i.e., different salts having the same anion or cation, the same valence type, etc., often produced widely different effects. The data obtained from powders containing various concentrations of inorganic salts suggested the hypothesis that the magnitude of the effect also depends on what may be called the *active concentration,* or *solubility,* of the salt in the powder, a quantity which is approximately equal to or less than the gross concentration. It also seemed probable that potassium nitrate, and perhaps other salts as well, enter catalytically into the gas evolution reactions.

Diphenylamine exerted a powerful inhibitory effect on gas evolution in the vacuum stability test as long as it was present in the powder, but the disappearance of this compound was accompanied by a normal or slightly higher rate of gas evolution.

A study of the property of ureas substituted with various combinations of ethyl and phenyl groups showed that the N,N′-diphenyl configuration may be associated with the greatest inhibitory effect on gas evolution in the vacuum stability test at 110 C.

The gases evolved from double-base powder during the vacuum stability test were analyzed; they consisted chiefly of carbon dioxide, nitric oxide, carbon monoxide, nitrogen, and nitrous oxide.[195] The composition of the gases varied considerably with both the temperature and the duration of the test.

The presence of water, acid, and nitroglycerin was demonstrated in the products which collected in the cooler portions of the vacuum stability units.

Special attention was given to a critical evaluation of the results of the vacuum stability as compared with other standard and special tests.[183] The vacuum stability test, in common with several standard tests which are used to evaluate the stability of smokeless powder, possesses the disadvantage that it is carried out at temperatures which are considerably above normal storage conditions and the special disadvantage that there is a marked tendency for the products of decomposition of the powder to distil into cooler portions of the unit and thus be removed from further interaction with the sample.

6.12.4 The Taliani-Type Test

In the Taliani test the powder sample is heated at constant volume in an initial atmosphere of air at atmospheric pressure, and the pressure which develops during the test is recorded as a function of the time of heating. A highly modified form of the Taliani apparatus was developed at the California Institute of Technology. The apparatus, experimental procedure, and some of the results obtained have been described.[196] Preliminary results indicate that this form of the Taliani test is suitable for routine testing of smokeless powder and that it may possess considerable advantage over the vacuum stability test in the evaluation of the relative stability of powders.

6.12.5 Measurements of pH

It has long been known that under ordinary storage conditions smokeless powders undergo gradual changes in composition and properties, often leading eventually to deterioration beyond the range of safe or effective use. It has also been known that these changes are accompanied by the development of acidity in the powders. A technique for the detection and measurement of this acidity would therefore be expected to be valuable in furnishing information relating to the stability of smokeless powders. Many such techniques have been proposed and applied. In general they have either made use of chemical indicators[187,197,198] or have involved the potentiometric estimation of hydrogen-ion concentration in a solution prepared from the powder sample.[199-202]

The method developed at the California Institute of Technology for studying the acidity of powders is based on the potentiometric method.[203] The pH of a suspension obtained when a given amount of water is added to an acetone solution of a powder sample is determined with a Beckman (Model G) pH meter. The method is more fundamental than many proposed earlier because the powder is completely dispersed during the course of the procedure. It is more flexible in its application because it prescribes no previous treatment for the powder sample. Furthermore, it is important to note that all operations relating to this test are performed at room temperature; in this respect it differs from the usual stability tests carried out on single- and double-base powders.

Some of the results obtained from the measurements of pH are summarized in the following paragraphs.

Captured German and Japanese propellants showed pH values which were considerably higher than those of standard U. S. powders. Most German propellants have values of about 8.0, Japanese propellants about 6.5, and U. S. propellants about 5.5 to 6.0. As a rule the foreign powders were found to contain significant amounts of alkaline earth elements.[106,107] It is very likely that their high pH values were due in large part to the presence of alkaline earth oxides or carbonates.

Measurements of pH were made on a group of modified ballistites[169] after various periods of heating at 65.5 and 71.0 C. All of the ballistites became increasingly acidic during storage at elevated temperature. Those which contained potassium nitrate showed lower pH values at all corresponding times of heating than did similar powders containing potassium sulfate. In those powders which contained potassium sulfate the substitution of diphenylamine for ethyl centralite seemed to increase the rate of decline of the pH value.

An examination of the effects of powder composition on pH value showed that most powders containing potassium nitrate showed lower pH values than powders of similar composition containing potassium sulfate. The reason for this effect is not well understood.

The stabilizers which were examined had no marked effect on pH value.

In connection with the study of foreign propellants it was noted that those powders which contained nitroglycerin were always more acidic than similar ones containing diethylene glycol dinitrate.

The nitrocellulose ingredient occasionally had a marked effect on the pH value of a powder, possibly because of some special treatment that the nitrocellulose had undergone.

It thus appears quite likely that the source and purity of powder ingredients are often the controlling factors in determining the pH value of powders. For this reason a measurement of pH alone cannot be informative, and therefore the pH test must be coupled with other stability tests to be most useful.

6.12.6 The Surveillance Test

The surveillance test at 65.5 C is a standard test in use by the Army and Navy for the estimation of the stability of propellent powders. In this test a forty-five-gram sample of the powder in a glass-stoppered bottle of a standard design is placed in a room or oven that is maintained constantly at a temperature of 65.5 C, and the sample is examined daily until red fumes are observed in the bottle, or until a specified minimum time has elapsed. This time in days is reported as the 65.5 C surveillance life of the propellant.

If this test is to be used as a means for detecting small differences in the relative stabilities of samples of powder, it is essential that all specimens be subjected to conditions which are as nearly identical as possible throughout the test. For this purpose a surveillance house was designed and constructed which provided for all samples storage conditions as nearly identical as practicable.[204] The house accommodates 1,000 bottles which are attached to a single endless chain belt which travels slowly on sprocket wheels over two concentric helical paths. The bottles are examined through a window located near the chain and can be introduced or removed through small access ports.

The great disadvantage of the surveillance test, particularly in experimental studies, is the length of time, sometimes amounting to a year or more, that is usually required for the completion of the test. Consequently many results of tests on powders of various compositions tested at the California Institute of Technology are not yet available. From the tests already completed,[183] however, the following conclusions were reached.

Powders containing diphenylformamide showed short surveillance lives (34 to 62 days). Powder contraining no stabilizer at all showed an extremely short surveillance life (14 days), in agreement with general experience.

Nitroglycerin powders containing ethyl centralite showed, in general, longer surveillance lives than analogous powders containing diphenylamine. Moreover an increase in the amount of centralite in a powder was found to prolong its surveillance life. Powders containing potassium nitrate showed shorter surveillance lives than powders containing potassium sulfate, and increases in the content of potassium nitrate resulted in decreases in surveillance life.

6.12.7 The Heat Test

The results of heat tests[205,206] on double-base powders[207] are in reasonably good agreement with the results obtained for the same powders in the vacuum stability test. The unusually long heat test times shown by powders containing nitroguanidine and either Fivonite or DINA may be due, in part, to the differences in composition of the gases evolved by these powders and by the more common double-base powders.

6.12.8 The Nitrogen Dioxide Stability Test

Some preliminary experiments were made on a stability test based on the reaction of nitrogen dioxide at room temperature with double-base powder. When a sample of powder was placed in a flask which contained a small concentration (about 25 mg per liter) of nitrogen dioxide, the concentration dropped rapidly to a very low value (0.1 mg per liter) and subsequently rose, at first slowly and then rapidly. Measurements[v] of the concentration were continued at regular time intervals until a high value was reached (10 mg per liter or more).

Although an examination of the preliminary data which were obtained suggested that the behavior of smokeless powder, when treated with nitrogen dioxide, may be made the basis of a stability test, much more work must be done before definite conclusions can be drawn. If successful, this test would possess the advantage that it could be performed quickly and that the powder would be at normal storage temperatures throughout the test.

6.12.9 Rocket Safe Test for Shipboard Use

At the request of the Navy Bureau of Ordnance, the development was undertaken of a means by which dangerous decomposition of a propellent charge in a rocket motor might be easily and quickly detected on shipboard or in the field. It was desired that the test be applicable to a rocket motor without destroying the usefulness of the round, that it be a test which untrained personnel on shipboard could perform and interpret, that it be applicable to all rocket motors in service, and that it make use of no indicators that are unable to withstand the severe conditions under which a shipboard test would ordinarily be used.

An unsuccessful attempt was made to develop a test based on measurements of the electrical conductivity of powder samples. A test that made use of the tarnishing of steel disks when they are exposed to fumes evolved by decomposing powder was investigated, but work on it was abandoned because the use of this test for every round would require the installation of an observation window in every rocket motor. Another test, which was partially investigated and which appeared to be promising, involved the withdrawal of a sample of gas from the rocket motor and the detection of gaseous decomposition products of the powder by bubbling the sample of the gas through a suitable indicator solution.

The test that was most extensively investigated depended upon the breaking of an electric circuit when corrosive fumes from powder undergoing decomposition severed a fine copper wire. An insulated unit carrying the wire is mounted in a hole in the nozzle closure of the rocket motor. External leads are provided for testing the circuit with a suitable indicating device.

A rough calibration of this test device was made by exposing it to known concentrations of nitrogen dioxide at different temperatures and different relative humidities. Preliminary experiments were made with stable and unstable powders, and several standard rocket rounds were fitted with the device for observation during normal storage.

When the investigation was terminated, much experimental work remained to be done before the copper wire safe test device could be recommended for routine use.[208]

6.12.9 Estimation of Available Nitrite in Smokeless Powder

Since the gases evolved by powders at elevated temperatures are known to contain various reduction products of nitrate, such as nitric oxide, nitrous oxide, and nitrogen, it might be expected that the heated powders themselves would contain nitrite ion or would yield nitrite ion when extracted with water. Such is indeed the case, and a procedure was worked out for the estimation of "available nitrite" in heated and unheated samples of double-base powder. Although it was not expected that the amount of available nitrite detected would be strictly equivalent to the amount of nitrite ion actually present in the powder, the available-nitrite content might perhaps give a relative measure of the extent of decomposition of the powder.

The procedure for the available-nitrite determination is based on a colorimetric method which is reproducible and is sensitive to about 0.3 part of nitrite per million parts of powder.[209]

Preliminary results indicate that the available-nitrite content of unheated, normal powder is not much greater than the limits of detectibility of the method, but that for heated samples of powder the nitrite content may be 1,000 times greater than for the unheated samples.

[v]The concentration measurements were made by means of a conductometric apparatus ("Egbert") which was developed by NDRC, Division 9.

6.13 THE PHYSICAL PROPERTIES OF SMOKELESS POWDERS[w]

In World War II, interest in the mechanical properties of smokeless powders has been greatly accentuated by the use of these propellants in rockets and similar devices, which has introduced quite new requirements as to strength and related characteristics. Knowledge regarding the effect of various factors upon these properties is even yet rather limited, since no complete and systematic investigation of this subject has previously been made. Many useful investigations were made in various laboratories of the effect of moisture content, of the effect of varying the amount of rolling, etc., but studies of the effect of composition have generally not been of the sort which would be expected to yield very fundamental information. For obvious reasons, such studies have usually been concerned with powder series in which only such changes were made as are compatible with a roughly constant potential. Unfortunately more than one factor has generally been varied at a time so that the results have been difficult of interpretation, and the general situation has not been clarified.

Since it seemed desirable to obtain more fundamental information regarding the effect of composition upon the mechanical properties of smokeless propellants, measuring equipment was developed at the California Institute of Technology under OSRD Contract OEMsr-881, and a program of investigation was laid out along lines described below. It seemed unprofitable for this laboratory to be concerned with structural factors involving particular shapes of propellent charges and their relation to the container or rocket motor. Studies of this sort were made in other laboratories, and it is understood that satisfactory progress was made in this direction. The object was rather to investigate those intrinsic properties of the propellant of which a knowledge might be of use in any future design work. The properties chosen for immediate study were hardness, as measured by the methods developed by A. G. Ward and co-workers,[210] and the so-called Young's modulus, or more exactly, the compression under a fixed load and subsequent recovery as a function of time.

A single apparatus was constructed which permitted the measurement of either hardness or Young's modulus merely by exchanging "anvils" and adjustment of the loading mechanism. The apparatus was designed to make measurements upon ¼-in. or ⅜-in. rod for the following reason. A systematic investigation may be presumed to require the study of a large number of special compositions which would be difficult to procure in large quantity. Measurements were consequently made upon materials extruded by the small press which is designed to deal with small experimental batches prepared at the California Institute of Technology (see Section 6.10).

It was the intention to study, so far as is possible, the effect of varying separately the various factors of composition which may be expected to affect the physical properties of a propellant. These factors were varied within sufficiently wide limits so that the resulting effects were well outside the limit of experimental error. The majority of powders of any given series were presumably impractical from the point of view of ballistics, but it was anticipated that by this procedure the situation would be more rapidly clarified than would be the case if one had attempted to keep within the range of practical compositions.

The phase of the investigation chosen for first study was the effect of the character of the nitrocellulose upon the physical properties of the propellant. In particular the following factors were studied: the effect of the source of the cellulose, whether wood pulp or cotton linters; the effect of varying the viscosity or average molecular weight of the nitrocellulose (the nitrogen content being kept constant); the effect of varying the nitrogen content of the nitrocellulose (the viscosity being kept constant); the effect of blending materials of different nitrogen contents and viscosities. This last phase was essentially a study of the effect of the heterogeneity of the nitrocellulose upon the properties of the propellant. The following blends were selected for investigation: a blend of high and low viscosity components having the same nitrogen content; a blend of high and low nitrogen components having the same viscosity; a blend of high nitrogen, high viscosity material with a second component of low nitrogen content and high viscosity; a blend of high nitrogen, high viscosity material with a second component of low viscosity and low nitrogen content. These blends were compared with homogeneous material having the average viscosity and nitrogen content of the blend. Blends of high nitrogen, low viscosity nitrocellulose with material of low nitrogen content and high viscosity would have been added to this list if suitable nitrocelluloses could have been obtained.

Several series of experimental powders embodying

[w]This section is taken from a summary prepared by Richard M. Badger.

the variations mentioned above were prepared for study. These were all made according to the JPH formulation given below and differed only in respect to the nitrocellulose constituent.

Formulation of Experimental Powders	
Nitrocellulose	54.5
Nitroglycerin	43.0
Ethyl centralite	1.00
Potassium sulfate	1.50
Carbon black (added)	0.20

Considerable time was devoted to establishing the conditions under which measurements were to be made and to determining a suitable routine of measurement. Any conditions of measurement chosen had to be somewhat arbitrary, but it was desirable, both that they be practical of attainment, and that they have some relation to the conditions under which propellants are normally conditioned and employed in practice. It was tentatively decided to make routine measurements at 25 C (77 F), and at 45 C (113 F) on powder samples which were adequately conditioned at 50 per cent relative humidity at 25 C. Powder samples to be measured at the higher temperature were brought to temperature under conditions such that loss of volatiles was presumed to be negligible. A provisional routine of measurements was worked out which appeared to be suitable for the materials under investigation.

These investigations provided many interesting results, but any conclusions arrived at are tentative. With one possible exception, the measurements of hardness and Young's modulus were found to run parallel. Because of lack of time for study of the data, no precise correlation was made. The most striking observation made is the extreme sensitivity of the mechanical properties of the propellant to the nitrogen content of the nitrocellulose. This sensitivity is so great that it may well contribute to the lack of perfect reproducibility of measurements from sample to sample. The effect of varying the viscosity of the nitrocellulose constituent was not very striking except in the range of very low viscosities. The effect of blending nitrocelluloses of different characteristics is not as yet entirely clear. In general the powders made from blended materials appeared to be somewhat harder at 25 C than those made from more homogeneous constituents, but they tended to have larger temperature coefficients of their physical properties. The effect of wood pulp versus cotton linter nitrocellulose was not definitely established at ordinary temperatures, but the wood-pulp material resembled a blend in respect to the temperature coefficient.

The investigations here briefly described are being continued at the California Institute of Technology under Contract NOrd-9652 with the Bureau of Ordnance of the Navy Department, and full reports will be given of the results obtained when various stages of the investigation are completed. It is expected that later studies will include the effect of the ratio of nitroglycerin to nitrocellulose, the effect of DEGN versus nitroglycerin, and the effect of plasticizers in relation to the nitrogen content of the nitrocellulose.

6.14 EXAMINATION OF FOREIGN PROPELLANTS[x]

From time to time the group working on Contract OEMsr-881 at the California Institute of Technology was requested to analyze samples of explosive material taken from captured rounds of German and Japanese ammunition. Most of these samples were propellent powders taken from rocket motors; a few, however, consisted of high-explosive materials taken from the warheads of shells and rockets, while other samples consisted of propellent powders for guns. The very unusual compositions of the rocket propellants and their excellent physical properties and burning characteristics provided opportunities for investigating the relationships between the composition and the properties of double-base powders and suggested possible methods of formulating rocket propellants superior in physical and burning properties to those now commonly used in U. S. rockets.

The foreign rocket and gun propellants were analyzed qualitatively and quantitatively for their major constituents, the nitrocellulose blends were examined, and the inorganic constituents were estimated. Several rocket propellants were examined with the microscope to obtain information concerning the methods of manufacture and were subjected to vacuum stability tests and measurements of pH. Their linear burning rates were measured at various temperatures and pressures and were compared with those of representative U. S. rocket propellants. The compositions of some of the propellants were used as starting points for the formulation and preparation of experimental powders in small batches of rolled sheet and dry-extruded grain; these experimental powders were

[x]This section is taken from a report submitted by David P. Shoemaker.

also subjected to tests in order to determine the extent to which the excellent physical and burning properties of the German and Japanese propellants were reproduced in these powders.

The results of these investigations have been described in OSRD reports.[106,107,211] The principal features of the work, chiefly with regard to the foreign rocket propellants, are discussed below.

6.14.1 Analysis of the Propellants

Each of the rocket propellants to be analyzed was finely divided and extracted with ether or with methylene chloride. The extract was analzed by chromatographic-spectrophotometric procedures (see Section 6.11). The residue from the extraction consisted principally of nitrocellulose but usually contained also inorganic substances and graphite or carbon black. The nitrocellulose was fractionated with 2/1 ether-alcohol or with methanol, and the fractions were analyzed for nitrogen by means of the nitrometer or by the Devarda procedure. The residue from the ether extraction was further extracted with water, and the resulting aqueous solution was analyzed for inorganic anions by polarographic procedures. Graphite and carbon black were estimated in the usual way, and metallic elements were estimated by a spectrographic procedure with the use of lithium as an internal standard; the identification of several of these inorganic constituents was aided by X-ray diffraction studies. The methods used in the examination of the nitrocellulose and in the identification and estimation of inorganic constituents have been described in Section 6.11.

The gun propellants were analyzed by procedures similar to those mentioned above. Previously established procedures were used in the determinations of such constituents as vaseline and nitroguanidine.

Measurements of pH were made on many of these powders in 1/1 acetone-water dispersions, and several of the rocket propellants were tested in the vacuum stability test at 110 C. The procedures for the vacuum stability tests and measurements of pH are described in Section 6.12.

All the foreign rocket propellants examined were double-base powders, apparently prepared by solventless processes. Microscopic examination of the grains of typical German and Japanese propellants indicated that the grains were dry-extruded from carpet rolls of sheet powder. Use of the polarizing microscope indicated the presence of both positively and negatively birefringent fibers, an observation which constitutes evidence that the grains contained a blend of at least two nitrocelluloses differing in nitrogen content.

Six German and five Japanese rocket propellants were examined.

German Rocket Propellants

21-cm rocket	28-cm rocket-assisted shell
15-cm high explosive rocket	ATO unit
15-cm incendiary rocket	1,000-kg jet-accelerated bomb

Japanese Rocket Propellants

20-cm naval rocket	20-cm army rocket
45-cm (17.5-in.) rocket (gray grains)	Suicide bomb (BAKA)
45-cm (17.5-in.) rocket (brown grains)	

In addition, gun propellants were examined for the German APC 50 mm shell, APC 88 mm shell, and APHV 50 mm shell; and the Japanese AT 37 mm shell.

The first five of the German propellants are closely related in composition and are markedly different from U. S. ballistites. They contain 30 to 35 per cent of DEGN as an explosive plasticizer in place of nitroglycerin, which is present in amounts of 40 to 43 per cent in U. S. ballistites. The German powders contain as stabilizers ethylphenylurethane, diphenylurethane, and acardite and contain graphite or carbon black as a darkening agent. The nitrocellulose in each is apparently a blend, one component of which is a high-nitrogen (about 13.0%) nitrocellulose having a moderate viscosity and the other a low-nitrogen (about 11.6%) nitrocellulose having a very low ("lacquer") viscosity. These powders show very high pH values in comparison to U. S. powders, and they contain significant amounts of magnesium or calcium; it appears likely that the alkaline earth metals are present as oxides or carbonates. The propellant from the ATO unit contains about one per cent of titanium dioxide (rutile).

The 1,000-kg bomb propellant differs considerably from the other German rocket propellants in composition; it contains nitroglycerin instead of DEGN, contains barium sulfate but only traces of magnesium or calcium, and has a pH value which is considerably lower than the values shown by the others but is higher than those of U. S. ballistites.

The Japanese rocket propellants are very different from the German powders in composition. They, too, contain blends of nitrocelluloses, but the nitrogen contents of the low-nitrogen components are much lower than in the German propellants. The Japanese propellants contain from 27 to 31 per cent of nitroglycerin and 3 to 5 per cent of ethyl centralite. In

addition, each propellant contains one additional compound as plasticizer or stabilizer: the 20-cm naval rocket propellant and the gray grains from the 45-cm rocket contain about 3 per cent of N-(*o*-tolyl)urethane, the BAKA propellant and the brown grains from the 45-cm rocket contain about 6.5 per cent of α-nitrophthalene, and the 20-cm army rocket propellant contains about 4 per cent of N,N-diphenylformamide. All the Japanese propellants except the brown BAKA propellant and the brown grains from the 45-cm rocket were gray in color and contain graphite or carbon black. All the propellants contain significant amounts of calcium, sodium, and silicious material; moreover, the BAKA propellant contains 3 to 4 per cent of potassium sulfate. The *p*H values of these propellants are intermediate between those of the German propellants and those of American ballistites.

Curiously enough, the motors of the Japanese 45-cm rockets contained a random selection of gray and brown grains of the compositions described above. Consequently, traces of α-nitronaphthalene were found in the gray propellant. The brown grains exhibit an interesting color difference which is discussed in connection with the burning rate studies.

The German gun propellants, like the rocket propellants, contain DEGN but in smaller amounts. One of them, the APC 88 mm shell propellant, contains in addition 32 per cent of nitroguanidine, 4 per cent of diphenylurethane, and 4 per cent of ethylphenylurethane. The APC 50 mm shell propellant contains nearly 8 per cent of ethyl centralite and more than 1 per cent of vaseline. The propellant from the Japanese AT 37 mm shell resembles the Japanese 20-cm army rocket propellant but contains a higher percentage of nitroglycerin, lower percentages of ethyl centralite and N,N-diphenylformamide, and a higher percentage of nitrogen in the nitrocellulose.

The sample of Japanese AT 37 mm shell propellant consisted of only four grams of material, and the entire analysis, including the identification of a previously unknown stabilizer as N,N-diphenylformamide, was carried out with that small amount of material. It was largely due to the successful development of chromatographic techniques for powder analysis that the identification of the unknown compound and the estimation of the stabilizers were possible.

In the vacuum stability test at 110 C, the German propellants evolved gas at rates that were much lower than the rate of gas evolution of ballistite JPN, but the Japanese 20-cm naval rocket propellant evolved gas much more rapidly than JPN. It is not possible to interpret these results unequivocally, largely because of the considerable differences in composition.

6.14.2 Investigations of Linear Burning Rates

Apparatus and Procedure

An apparatus similar in many respects to that of Crawford[212] was used for making measurements of linear burning rate on foreign propellants and various experimental powders. Its construction and the procedure for its use have been described in detail.[123] Since this apparatus has been very useful in obtaining burning rate data at high pressures with the use of small amounts of powder, it may be worth while to describe it briefly here.

The burning rate bomb, a pressure vessel of stainless steel, is equipped with a closure plug incorporating an unsupported-area seal. The use of this seal obviates the need of a wrench for opening or closing the bomb. The powder support, which is mounted on the inner surface of the closure plug, carries a powder clamp and five pairs of binding posts. The uppermost pair of posts carry the ignition wire; the other four pairs are terminals for four fusible wires. Electric connections to external circuits are made through insulators in the closure plug. The bomb is connected to a source of nitrogen at high pressure and also to a tank which is used as a reservoir to increase the volume of the system and render the conditions more nearly isobaric. The bomb is situated in a water bath for temperature control. An electronic timing circuit, incorporating three clocks graduated to 0.01 second, is used to determine the relative times at which the four fuse wires are burned out by the ignited powder strand.

The powder is tested in the form of $\frac{3}{32}$-in. cylindrical strands which are usually prepared from carpet-rolled sheet powder or from shavings of grain powder by extrusion through a $\frac{3}{32}$-in. die in a one-inch extrusion press. The strands are cut into 18-cm lengths. To insure end-burning of the strands, each length is dipped twice in a 5% dispersion of polyvinyl alcohol in water; the strands are allowed to dry after each dipping. Four holes, spaced at 5-cm intervals, are drilled in each stand with a No. 78 drill, short lengths of ½-ampere fuse wire are inserted through the holes, and the strand is given a third dipping and allowed to dry.

In preparation for each burning rate measurement, the strand is clamped to the powder support, the ends of the fuse wires are fastened to the binding posts, the closure plug is screwed in place, and nitrogen is admitted to the desired pressure. After the system has come to thermal equilibrium, the strand is ignited at its upper end by electrically heating the ignition wire. When the flame burns out the first fuse wire the three electric clocks are started simultaneously and automatically. As the flame burns out the second, third, and fourth fuse wires the first, second, and third clocks, respectively, are automatically stopped. The three burning intervals are compared in order to detect any irregularities in burning, and their sum is used in the calculation of the linear burning rate.

Burning rate measurements are made at pressures ranging from 400 to 1,900 psi and at temperatures ranging from 0 to 50 C. Usually the burning rate data obtained at each of two or three different temperatures are plotted against pressure, and a smooth curve is drawn to represent the variation of burning rate with pressure at each temperature. From curves obtained in this way several quantities may be derived which are of considerable interest with regard to the suitability of the powder as a rocket propellant. These quantities are the pressure index (the quantity n in the equation $r = p^n$, where r is the linear burning rate at a given temperature and p is the pressure), the temperature coefficient of linear burning rate at a given temperature and pressure, and the temperature coefficient of steady-state pressure in a hypothetical rocket motor at a given temperature, calculated for each of several representative pressures.

Results

The results of measurements of burning rate on the propellant from the German 21-cm rocket are plotted in Figure 14. This propellant is unusual for its comparatively low burning rate (less than half that of JPN), and for its small dependence of burning rate on pressure and temperature. Although the burning rate of this German propellant is much less dependent on temperature and pressure than is that of U. S. ballistite, the German 1,000-kg bomb propellant gave even higher values of the pressure index and the temperature coefficient of steady-state pressure than were given by ballistite.

There is an inflection at about 550 psi in the burning rate curve for the German 21-cm rocket propellant at 25 C, and a more pronounced one at about 650 psi in the curve for 50 C. Only a weak inflection is ob-

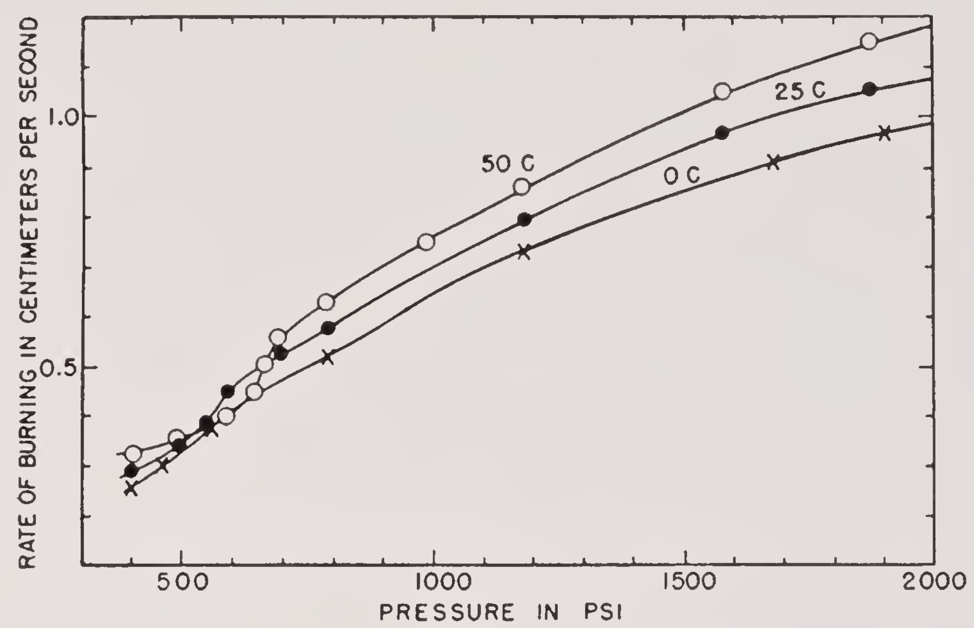


Figure 14. The burning rate of the propellant taken from a German 21-cm rocket.

servable in the curve for 0 C. The presence of the inflection in the burning rate curve probably indicates a difference in the burning mechanisms below and above the pressure corresponding to the inflection. A much more pronounced inflection has been observed in measurements of the burning rate of a sample of the propellant from the German 28-cm rocket-assisted shell. Although the phenomenon in both cases is certainly real, it is by no means uniform; other samples of both the 21-cm rocket propellant and the 28-cm rocket-assisted shell propellant have failed to show these inflections.

By far the best of the foreign powders studied was the propellant from the Japanese 20-cm naval rocket. This propellant had a burning rate comparable to that of the German 21-cm rocket propellant, but had the smallest pressure and temperature coefficients of burning rate observed for any of the powders.

The brown propellant from the Japanese 45-cm rocket also has a low burning rate and low pressure and temperature coefficients. This propellant exhibits the following very curious phenomenon. When the propellent grain is sectioned, it is observed that the material within one centimeter of the periphery and also the material within the same distance of the central perforation are brown in color and are translucent, while the remaining material is tan in color and is opaque. There appears to be no difference in composition between the tan and brown materials; moreover the tan material is transformed into the brown material gradually on standing and more rapidly when rolled at elevated temperatures. The burning rates of both materials were measured; in order to obtain strands of the tan material for use in the burning rate studies, it was necessary to extrude chips cut from the grain rather than carpet-rolled sheets

prepared from such chips by the usual procedure. At temperatures below 45 C the tan material burns more slowly than the brown, and the brown material has the lower values of the temperature coefficients of linear burning rate and of steady-state pressure.

Attempts to duplicate this material yielded lemon-yellow, translucent grains that showed no tendency to exist in more than one modification. Hence the cause of the existence of both tan and brown material is completely unknown. Moreover, since the difference in linear burning rate between the brown and tan portions of the propellent grain would be expected to result in markedly regressive burning of the grain, it is difficult to understand the advantage to be gained by the manufacture of grains having this structure, if indeed the existence of this structure is not accidental. The phenomenon appears to be general; the differences in color were observed in grains taken from two different rockets of the same type. A somewhat similar, though less pronounced, color difference was observed on examination of the propellant from the Japanese BAKA bomb.

6.14.3 The Preparation of Experimental Powders

Because of the excellent physical properties and burning characteristics of the foreign propellants, it was hoped that knowledge gained from studying these propellants could be applied successfully to the formulation of propellants superior to existing U. S. rocket propellants in physical and burning properties. In order to supplement the information gained from analytical studies and burning rate measurements and to determine ways in which American propellants with improved properties could be made, experimental powders were made up in five-gram batches of rolled sheet and in sixty-gram batches of sheet or of dry-extruded grain. Commercially available materials were used in the preparation of these powders which, for the most part, were formulated on compositions resembling those indicated by the analyses of the propellants from the German 21-cm rocket, the Japanese 20-cm naval rocket, and the Japanese 45-cm rocket.

The powders that were prepared on compositions resembling that of the German 21-cm rocket propellant had excellent physical properties, equaling or even surpassing those of the German propellant. However, they did not exhibit the low pressure and temperature dependence of burning rate shown by the German propellant. Likewise, attempts to duplicate the excellent burning properties of the Japanese propellants were not successful. It has already been mentioned that the powders prepared on a composition similar to that of the brown grains from the Japanese 45-cm rocket did not have the peculiar structure of that propellant.

It is demonstrated by these results that the chemical analyses of the foreign propellants did not lead to their complete characterization. The results of some experiments described elsewhere indicate that the constituents responsible for the excellent burning properties of the foreign propellants reside mainly in their ether-insoluble parts. These constituents may be the nitrocellulose blends, or their components, to which desirable characteristics may have been imparted by techniques unknown in this country. Certainly the procedures now available for the examination of the nitrocellulose in a powder do not provide a characterization nearly complete enough to permit the duplication of the nitrocellulose in all of its properties. Hence, with the analytical techniques now at hand, the practical limit of usefulness of the kind of experiments described above has been approached, and it appears that further information can be gained only by means of experiments along new lines.

The capitulation of Germany and the consequent revelation of German technical secrets has afforded opportunities, much greater than those afforded by the capture of isolated enemy propellants, for the formulation of improved propellants for U. S. rockets. The techniques for the preparation and testing of small batches of experimental double-base powder might be expected to find ready application in studies of rocket propellent compositions discovered by Allied investigators in Germany as a result of their interrogation of German technical personnel. Indeed, these techniques have been successfully applied to a study of the "Einheits Pulver" rocket propellent composition,[213] a standard composition intended for universal production in Germany during the last year or two of the war in Europe. The experiments made on the Einheits composition were the most fruitful of any of the experiments made on foreign rocket propellent compositions at the California Institute of Technology.

The Einheits composition resembles the composition of the German 21-cm rocket propellant in many respects, but it contains, in addition to the compounds positively identified in the analysis of the 21-cm rocket propellant, the following constituents: 0.2% magnesium oxide, 0.6% potassium nitrate, and

1.5% hydrocellulose. Moreover it contains Acardite II (N,N-diphenyl-N′-methylurea) in place of Acardite I (acardite, N,N-diphenylurea). Experimental powders prepared at the California Institute of Technology on compositions resembling the Einheits composition equaled or surpassed in burning characteristics all the foreign propellants studied in that laboratory. The experiments indicated that the presence of hydrocellulose, potassium nitrate, and magnesium oxide together was the factor chiefly responsible for the extraordinarily low temperature and pressure dependence of burning rate of the Einheits-type powders.

It does not follow, however, from consideration of the excellent burning characteristics of the German 21-cm rocket propellant that this propellant must contain hydrocellulose and potassium nitrate. It does not seem very likely that both these substances could have escaped detection if they were present in the propellant.

Some further experiments have indicated that the inclusion of potassium nitrate, hydrocellulose, and magnesium oxide in certain powders of low potential (such as modified German-type powders, Japanese-type powders, and H-4 powders) significantly lowers the dependence of burning rate on temperature and pressure. No beneficial effects have been obtained from experiments in which these three materials were incorporated in high-potential ballistite such as JPH.

The experiments described above give considerable promise of pointing the way toward the formulation of improved rocket-propellent compositions. If these experiments are continued and extended, an understanding of the nature of the effects of hydrocellulose, potassium nitrate, and magnesium oxide may perhaps be gained, with the possible result that other and better methods may be found for improving the burning characteristics of rocket-propellent powders.

6.15 MISCELLANEOUS

A variety of miscellaneous activities of Division 8 having to do more or less directly with propellants can be mentioned briefly in this section.

Two studies have been made of the thermochemical properties of propellants. The first[214] presents data on both commercial and experimental compositions; the second[215] presents data on Albanite and related powders, on Cordite N, and on a number of RDX propellants. Since it was found that in some compositions the calculated values for the heat of explosion (obtained from the summation of the heat values of the individual ingredients) differed appreciably from the observed values, it was recommended that calorimetric measurements be made a part of any future research program on propellants.

The partial burning of propellants and of nitrocellulose has also been studied. An apparatus, consisting essentially of a high-pressure bomb fitted with a bursting diaphragm, was developed for this purpose. Photographs of grains partially burned in the bomb illustrate flaws in propellants. The apparatus should be of use both in the study of experimental compositions and as a control of quality in the production of propellent grains.[216,217]

Work on the partial burning of nitrocellulose began with the observations made at the Ballistic Research Laboratory, Aberdeen Proving Ground, that nitrocellulose when decomposed under reduced pressure yields a *red substance* (RS) and a *white substance* (WS). Division 8 was asked to determine the composition of these products, which it was thought might be of significance in an understanding of the mechanism of burning of nitrocellulose.

The red substance is a liquid obtained when nitrocellulose undergoes thermal decomposition at about 100 mm pressure. The yield of RS amounts to 35 to 40% of the weight of the nitrocellulose decomposed. RS has been analyzed for formaldehyde, glyoxal, formic acid, water, acetic acid, ethyl acetate, nitrous acid, and nitric acid. These constituents account for 80 to 90% by weight of the RS. Glyoxal, formaldehyde, formic acid, and water are considered to be the significant decomposition products. The first two are present in approximately equimolar amounts; significantly smaller molar amounts of formaldehyde and significantly larger molar amounts of water are present.

The white substance is an amorphous powdery solid, obtained when nitrocellulose undergoes thermal decomposition at pressures below 10 mm. The yield of WS amounts to 65 to 70% of the weight of nitrocellulose decomposed. WS is apparently a complex mixture. It gives a positive iodoform test, positive aldehyde tests, and liberates iodine from potassium iodide. WS decomposes more or less rapidly in solution; no soluble decomposition products have been isolated, but carbon monoxide, nitrous oxide, and nitrogen have been identified among the gaseous products. On heating crude WS with hydrochloric acid, carbon dioxide, furfural, nitrous and nitric acids are formed.[218]

Further work with crude WS showed that it could be purified by solution in methanol and precipitation with ether, followed by washing with water. The yield in this purification is 40%. The nature of the material lost in the purification is not known. The purified white substance (PWS), on the basis of analytical data and chemical reactions, is a mixture of closely related substances of very similar degrees of polymerization—average molecular weight about 1,500—with similar but not identical distributions of substituents.[219]

Work on the decomposition of cellulose nitrate under reduced pressure was transferred from Division 8 to the Ordnance Department on February 28, 1945.

Although Division 8, other than through its contract at the California Institute of Technology, did not devote much time to work with conventional double-base powders, some work on these powders was done at the Explosives Research Laboratory.

At the request of Division 3, Section H, a solventless cordite extrusion press was set up at the Explosives Research Laboratory of Division 8 at Bruceton, Pennsylvania. The press was used for the extrusion of propellent grains desired by the groups working on rockets, and a study was made of the factors affecting successful extrusion.[220-222] Essentially, this press was a service unit for the groups working on rockets at a time when it was difficult to secure solventless cordite grains for use in rockets. After these grains became available elsewhere, the apparatus was used for pressing experimental 8.5-in. diameter grains of composite propellant (Section 6.2).

A study of methods of inhibiting the burning of double-base propellants by the use of restrictive coatings has shown that copper- or silver-plated coatings are unsatisfactory because they separate from the grain on temperature cycling. The use of cellulose coatings was more promising, but the work with this material was not taken beyond a preliminary stage.[223]

Because the separation of nitroglycerin from double-base powders represents a potential hazard, a survey of the literature on this subject was prepared and an experimental study of the problem was outlined and started. The termination of the work of Division 8 took place before this experimental program was completed. The principal conclusion from the work was that there is little danger of the separation of nitroglycerin from modern double-base powders at low temperature.[224,225]

A completely different problem was that of developing a chemical igniter system for jet-propulsion devices employing fuming nitric acid-gasoline as fuel. Examination of a variety of materials led to the selection of a turpentine solution containing 30% by volume of du Pont SDO (a divinylacetylene polymer), inhibited with 1% of 2,6-di-*t*-butyl-4-methylphenol, as the initiator of choice. The operating procedure is to introduce the nitric acid and initiator into the motor, then to introduce the gasoline, and stop the flow of initiator. Operating and egnineering details are given in the original reports.[226,227]

Considerable synthetic organic chemical work was done at the California Institute of Technology where it was necessary to prepare small amounts of a number of compounds in connection with the research program on propellants.[228] The following new compounds were synthesized:

N,N-Diphenyl-N′-ethylurea	4-Nitro-N-ethylcarbanilide
N,N′-Diethyl-N-phenylurea	4-Nitro-N′-ethylcarbanilide
N-Phenyl-N,N′,N′-triethylurea	2,4,4′-Trinitrocentralite
2-Nitro-N-ethylcarbanilyl chloride	4-Nitro-N-ethyl-N-phenylbenzamide
2-Nitrocentralite	4-Amino-N-ethyl-N-phenylbenzamide
4-Nitro-N-ethylcarbanilyl chloride	4-(N-Ethylamino)-N-ethyl-N-phenylbenzamide

The following compounds had been prepared previously. Newer improved syntheses have been devised for them or new and interesting properties have been observed.

N,N-Diphenylcarbamic anhydride	4-(N-Ethylamino)-azobenzene
N-Ethyl-N′-phenylurea	N-Nitroso-4-nitrodiphenylamine
N-Ethyl-N,N′,N′-triphenylurea	N-Nitrosodinitrodiphenylamine
4-Nitrocentralite	2,2′,4-Trinitrodiphenylamine
Phthalide	Tetraphenylhydrazine
4-Nitrocatechol	N-(*o*-Tolyl)-urethane
1,3-Diphenyl-3-ethyltriazene	Phosgene-triethylamine complex

Attempts to inhibit the 32-degree transition of ammonium nitrate were not successful.[229]

Chapter 7

TRACERS AND IGNITERS[a]

Research on tracers by Division 8 was begun in June 1943 under Project NO-151 at the Explosives Research Laboratory [ERL]. Very little attention was paid in this work to the possibility of using tracer systems other than strontium nitrate-magnesium. The emphasis in the work was on methods of incorporating and loading this particular mixture and on attempts to determine the factors responsible for the behavior of tracers.

Because of the extensive experience with thermoplastic resinous binders in the preparation of molded composite propellants (see Section 6.2), particular attention was given to the use of these binders in making up tracers. It was found that by incorporating these resinous binders in edge-runner mills, tracer compositions with good molding properties could be obtained. However, these compositions functioned poorly when they were loaded at pressures below 50,000 psi. The conventional wax binders, it was also shown, could be incorporated in edge-runner mills, but adequate test data on the compositions prepared in this way are not available.

As shown by experience elsewhere, a layer of wax between the tracer composition and the shell markedly improves tracer performance. Similarly, the incorporation of organic fuels into the tracer mixture resulted in better performance. The number of blowouts was reduced, the color of the tracer was intensified, and the burning time was increased.

One of the great needs in tracer research is the development of static tests which can be carried out in the laboratory and whose results can be correlated with tracer performance. A start in this direction was made at the Explosives Research Laboratory by the construction of a bomb which permitted static firing of tracers so that ignitability, blowouts, and other phenomena could be studied. The results obtained with the bomb could not be correlated exactly with the results of gun tests, but the results with the bomb proved very useful.

During the course of the work on tracers at ERL a number of miscellaneous observations were made about tracer behavior. These observations, together with the speculations to which they led, and the experimental work described in the preceding paragraphs are reported in reference 1.

A much more far-reaching and comprehensive program on tracers was initiated under Projects NO-151 and OD-159 at the Metal and Thermit Corporation in November 1943. As a preliminary to the experimental work a review of U. S., British, and Canadian work on tracers was prepared.[2] All the experimental work done by the Metal and Thermit Corporation, together with the conclusions drawn from that work have been given in detail in a report which should be examined carefully by anyone interested in the subject.[3] Because of the varied nature of the investigations and the number of anomalies and complications which were encountered, it is feasible only to mention briefly a few of the items which were considered in the study and described in the report.

A review is presented of all the factors which influence the ignitability of an igniter and of the static tests used to measure this property. Two types of tests to measure ignitability have been evaluated experimentally, but it has been concluded that neither one gave adequate correlation with performance in a gun. Burning characteristics and heats of reaction of igniter compositions have been determined, and consideration has been given to the relation of these and other factors to the burning time of an igniter and its ability to transfer burning to the tracer composition.

Because of the poor storage characteristics of tracer ammunition under conditions of high temperature and humidity, attention was given to all the factors influencing the stability of igniters. Although there are many factors which influence the useful life of an igniter composition, all the experimental work of the contractor was devoted to the improvement of the chemical stability of the mixture itself. It was demonstrated in the laboratory that it should be possible to improve greatly the storage life of tracer ammunition containing standard bright igniters by employing either, or preferably both, of the following modifications.

1. The corrosion resistance of the magnesium can be increased by treating the surface with a dichromate wash or with an organic dye. Even better stability is

[a]This chapter is based on a summary prepared by S. R. Aspinall.

obtained by replacing magnesium with a surface treated magnesium-aluminum alloy.

2. The asphaltum binder, which actually accelerates the decomposition of the metal and peroxide, should be replaced with calcium resinate or some other binder which exerts a strong protective effect.

There is less standardization and less experience with dark or dim igniters, but certain tentative conclusions have been drawn which should lead to enhanced stability of such igniters.

For a variety of operational reasons, there have been established from time to time a number of requirements for tracer ammunition having a dim igniter. A detailed study was made of compositions which function as dim igniters, with primary emphasis on obtaining a mixture having a burning distance of 400 yards in the Mark 11 40 mm tracer. On the basis of preliminary gun trials, it was concluded that a mixture of manganese-barium peroxide binder shows considerable promise as a dim igniter.

A similar study of tracer compositions has been made. The question of tracer visibility is extremely complex, involving, among other things, psychological factors which are difficult to evaluate, but some information has been obtained on this subject. Chemical instability of tracer compositions leads to serious tracer malfunction, but the problem is less severe than with igniter compositions because the tracer compositions are inherently more stable and are protected from moisture by the igniter composition. However, improvements can be made by modification of the metal and binder (for the same reasons as indicated for igniters), and the hygroscopicity of specification grade strontium nitrate may be sharply reduced by a water wash. The effects of composition, physical state, loading technique, and tracer cavity dimensions on consolidation have been discussed.

By use of the Explosives Research Laboratory bomb mentioned above, an extensive laboratory study was made of blowouts and prematures. These very complex phenomena are not well understood in spite of the large amount of information obtained during this work and by previous investigators.

An entirely different aspect of the work in this field was the development of methods for the identification and analysis of primer compositions. These methods had to be rapid in their application and they had to be applicable to quite small amounts of material. Two procedures were developed. Polarographic analysis permitted the quantitative analysis of 100-mg samples of primer mixtures for antimonous sulfide, cuprous thiocyanate, lead azide, mercuric fulminate, and potassium chlorate.[4]

A qualitative analysis for 29 primer constituents was developed which was based on the optical and crystallographic constants of the individual compounds and in their behavior with selected chemical reagents. Reference data and procedures are given in the original report.[5]

GLOSSARY[a]

ACARDITE. Unsymm. diphenylurea.
AL. Aluminum.
ALUMATOL. AN/TNT/Al.
AMATEX. RDX/TNT/Al.
AMATOL. AN/TNT.
AN. Ammonium nitrate.
ANHYDROENNEAHEPTITOL PENTANITRATE.

$$\begin{array}{ll} CH_2\text{—}C(CH_2ONO_2)_2 & \\ | \quad\quad | & \\ O \quad\quad CHONO_2 & \\ | \quad\quad | & \\ CH_2\text{—}C(CH_2ONO_2)_2 & \end{array}$$

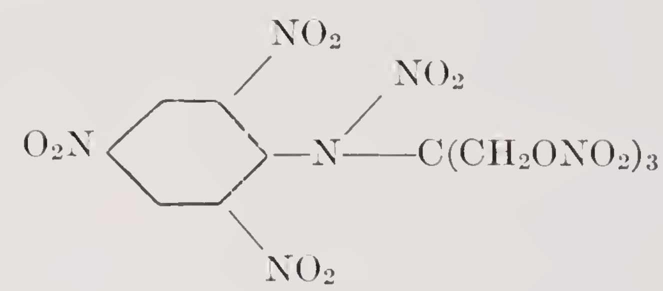
ASC BOMB. Antisubmarine shaped-charge bomb.
ASCFT BOMB. Antisubmarine shaped-charge follow through bomb.
ATO. Assisted take-off.
BARONAL. $Ba(NO_3)_2$/TNT/Al-50/35/15.
BEANO. A spherical hand grenade.
BSX.

$$\begin{array}{c} \quad\quad NO_2 \quad\quad NO_2 \quad\quad NO_2 \\ \quad\quad | \quad\quad\quad | \quad\quad\quad | \\ CH_3CO_2CH_2N\text{—}CH_2N\text{—}CH_2N\text{—}CH_2OCOCH_3 \end{array}$$

ButylNENA. $C_4H_9N(NO_2)CH_2CH_2ONO_2$
CAST DOUBLE-BASE POWDER.
Type O. Castings made from grains of double-base powder to which nitroglycerin and a non-volatile solvent have been added.
Type I. Like type O, but containing rate control strands of solvent-extruded composite propellant.
Type II. Like type O, but containing uniformly distributed rate control grains.
COMPOSITION A. A desensitized RDX having the usual composition RDX/wax-91/9.
COMPOSITION B. 60/40/1—RDX/TNT/wax.
COMPOSITION C. The American name for PE-2.
COMPOSITION C-2; COMPOSITION C-3. American PE's consisting of RDX plasticized with nitrotoluenes and thickened with nitrocellulose.
CORDITE N. A flashless double-base propellant containing about 55% of nitroguanidine.
CyclohexylNENA. $C_6H_{11}N(NO_2)CH_2CH_2ONO_2$.
CYCLONITE. See RDX.
CYCLOTOL. A castable mixture of RDX and TNT, e.g., 65/35 Cyclotol which is RDX/TNT-65/35.
D-1. A desensitizer for high explosives. The composition is paraffin/nitrocellulose/lecithin-84/14/2.
D-2. A modification of D-1 in which a higher-melting paraffin is used.
DDP. DINA/Dibutyl phthalate/centralite-85.5/10/1.5.
DEGN. Diethylene glycol dinitrate.
DENTEX. RDX/DNT/A1-48/34/18.
DINA. *bis*(β-Nitroxyethyl)nitramine.
DIPEHN. Dipentaerythritol hexanitrate.
DNP. 2,4-Dinitrophenol.

$$\begin{array}{l} \quad\quad\quad\; CH_2\text{—}N\text{——}CH_2 \\ \quad\quad\quad\quad | \quad\quad | \quad\quad | \\ \text{DPT.} \quad O_2N\;N \quad\; CH_2 \quad N\;NO_2 \\ \quad\quad\quad\quad | \quad\quad | \quad\quad | \\ \quad\quad\quad\; CH_2\text{—}N\text{——}CH_2 \end{array}$$

EDNA. See Haleite.
EDNATOL. A mixture of Haleite and TNT.
ERL. Explosives Research Laboratory, the central laboratory of Division 8, located at Bruceton, Pa.
EXPLOSIVE D. Ammonium picrate.
FIVONITE. Tetramethylolcyclopentanone tetranitrate.
FNH. Flashless nonhygroscopic.
FUME-OFF. The oxidative destruction of byproducts in nitration reactions.
H-4 POWDER. A ballistite type rocket powder (58% nitrocellulose, 30% nitroglycerin, 2.5% dinitrotoluene, 8% ethyl centralite, and 1.5% potassium sulfate) which is cooler and slower burning than JPN or JPT.
HALEITE. Ethylenedinitramine.
HBX. Torpex containing 5% of D-2.
H.E.A.T. High explosive anti-tank.
HEPTRYL.



HEXAMINE. Hexamethylenetetramine.
HEXANITE. Hexanitrodiphenylamine.
HEXOGEN. See RDX.
HMX. Cyclotetramethylenetetranitramine, a high explosive obtained by the nitrolysis of hexamine in the presence of acetic anhydride.
HVAR. High-velocity aircraft rocket.
JP (also JPH, JPN, JPT, JP 204). This abbreviation, followed by another letter or by a number, e.g. JPH, JPN, JPT, JP 204, refers to ballistic type rocket powders. JPT, for example, has the composition: 59% nitrocellulose (13.25% nitrogen), 40% nitroglycerin, and 1% ethyl centralite, to which are added 0.2% of diphenylamine and 0.1% of nigrosine dye.
MethylNENO. $CH_3N(NO_2)CH_2CH_2ONO_2$.
MINOL. TNT/AN/Al. A typical composition is 40/40/20.
MNO.

$$\begin{array}{l} CON(NO_2)CH_3 \\ | \\ CON(NO_2)CH_3 \end{array}$$

NENA. β-Nitroxyethylnitramine $O_2NOCH_2CH_2NHNO_2$.
NENO.

$$\begin{array}{l} CON(NO_2)CH_2CH_2ONO_2 \\ | \\ CON(NO_2)CH_2CH_2ONO_2 \end{array}$$

NIP. Nitroindene polymer.
OXYNITRATION. The direct conversion of benzene to dinitrophenol or picric acid.
PA. Picric acid.
PE. Penetaerythritol $C(CH_2OH)_4$. The same abbreviation is also used for plastic explosive.
PE-I. A British plastic explosive of the composition RDX/PE oil—88/12. The PE oil (plastic explosive oil) consists of 10% of crepe rubber in a 2:1 vaseline/paraffin oil base.
PE-2. A British plastic explosive of the composition 88/12-RDX/PE oil. The PE oil consists of vaseline/paraffin oil/lecithin—110/55/10.
PENTOLITE. A castable mixture of PETN and TNT. The most generally used composition is 50/50.
PENTONAL. PETN/TNT/Al 47/33/20.

[a]This glossary includes only those terms and abbreviations which are not in the standard books on explosives and which are not defined in the text of the Summary Technical Report.

PEP-2. A plastic explosive of the composition PETN/Gulf Crown Oil E-85/15.

PEP-3. Like PEP-2, but having the composition PETN/Gulf Crown Oil E-86/14.

PETN. Pentaerythritol tetranitrate.

Picratol. A mixture of PA and TNT.

PIPE. An insensitive plastic explosive of the composition PETN/Gulf Crown Oil E-81/19.

PNL. See D-1.

Pressure Exponent. The exponent n in the formula, $R = bp^n$, which describes the pressure dependence of the burning rate of a propellant.

PTX-1. RDX/tetryl/TNT. A typical composition is 30/50/20.

PTX-2. PETN/RDX/TNT. 25/44/28.

RDX. Cyclotrimethylenetrinitramine, a high explosive obtained by the nitrolysis of hexamine.

RDX(B). The mixture of RDX and HMX obtained by the combination process.

RDX Polar PE. A plastic explosive for use at low temperatures. The composition is RDX/oil = 88/12. The oil is a 95/5 mixture of Gulf 300 Process Oil and lecithin.

RIPE. An insensitive plastic explosive of the composition RDX/Gulf Crown Oil E-85/15.

RPL. Radford Pilot Lot, from Radford Ordnance Plant.

Schneiderite. Dinitronaphthalene (mixture)/AN-87/13.

Sixolite. Tetramethylolcyclohexanol pentanitrate.

Specific Impulse. The thrust in pound-seconds per pound of propellant delivered by a rocket propellant.

Temperature Coefficient of Propellants. The change in the pressure, thrust, and burning time of a propellant with change in initial temperature.

Tetrytol. Tetryl/TNT.

TNB. 1,3,5-Trinitrobenzene.

TNEB. 2,4,6-Trinitro-1-ethylbenzene.

Torpex-2. RDX/TNT/Al-42/40/18.

Trimonite. 1-Nitronaphthalene/PA-12/88.

Tritonal. TNT/aluminum mixtures; e.g. 80/20 Tritonal is TNT/Al-80/20.

UE. Underwater Explosive. A synonym for Tritonal.

BIBLIOGRAPHY

Numbers such as Div. 8-101-M1 indicate that the document listed has been microfilmed and that its title appears in the microfilm index printed in a separate volume. For access to the index volume and to the microfilm, consult the Army or Navy agency listed on the reverse of the half-title page.

The following brief description of the system used by Division 8 for reporting the results of its work should be of assistance to those users of this Summary Technical Report who have occasion to go beyond the summary to the original reports.

Division 8 has issued two types of reports: Interim Reports and OSRD Reports. Interim Reports were issued approximately monthly. Their purpose was to make available as quickly as possible to interested and qualified persons in the United States and the British Empire the results of investigations under way in the Division. Every contractor was required to submit a monthly report on his work; all the reports in each field of work formed the monthly Interim Report in that field. The information in the Interim Reports is tentative and subject to revision. The OSRD reports are also based on contractors' reports; but each OSRD Report deals, almost without exception, with the work of a single contractor. Each contractor was required to submit a report on his work, either at six-month intervals or on completion of a unit of the assignment; the OSRD report is constructed from the contractor's report.

The list which follows gives the various series of Interim Reports issued by Division 8. The letters preceding each series form the abbreviation used in referring to the series in the Technical Summary. Thus, the reference SC-1, Aug. 15 to Sept. 15, 1943, refers to the first issue of the Division 8 Interim Reports on shaped charges.

INTERIM REPORTS

CF *Controlled Fragmentation and Shaped Charges*, Numbers 1, Aug. 15 to Sept. 15, 1942, through 13, July 15 to Aug. 15, 1943.

DFA *Detonation, Fragmentation, and Air Blast*, Numbers 1, Aug. 15 to Sept. 15, 1943, through 20, July 15 to Aug. 15, 1945.

FS *Fundamental Study of Explosives*, Numbers 1, Aug. 15, to Sept. 15, 1942, through 13, July 15 to Aug. 15, 1943.

JP *Propellants for Special Jet Propulsion Devices*, Numbers 1, Aug. 15, to Sept. 15, 1944, through 12, July 15 to Aug. 15, 1945.

MK 29 *Mark 29 Device*, Numbers 1, Nov. 15 to Dec. 15, 1942, through 9, Sept. 15 to Oct. 15, 1943.

ODP *Organic Development Problems*, Numbers 1, Nov. 15 to Dec. 15, 1942, through 27, Jan. 15 to Feb. 15, 1945.

PT *Preparation and Testing of Explosives*, Numbers 1, Aug. 15, to Sept. 15, 1942, through 36, July 15 to Aug. 15, 1945.

RP *Rocket Propellants*, Numbers 1, Aug. 15 to Sept. 15, 1942, through 36, July 15 to Aug. 15, 1945.

RRC *RDX and Related Compounds*, Numbers 1, Dec. 15, 1942 to Jan. 15, 1943, through 22, Sept. 15 to Oct. 15, 1944.

SC *Shaped Charges*, Numbers 1, Aug. 15 to Sept. 15, 1943, through 24, July 15 to Aug. 15, 1945.

SP *Special Propellants*, Numbers 1, Aug. 15 to Sept. 15, 1942, through 35, July 15 to Aug. 15, 1945.

TC *Tracer Compositions*, Numbers 1, May 15 to June 15, 1943, through 18, July 15 to Aug. 15, 1945.

UE *Underwater Explosives and Explosions*, Numbers 1, Aug. 15 to Sept. 15, 1942, through 21, Apr. 15 to May 15, 1944. Beginning with Number 22 this series of reports was issued by Division 2.

As a guide to the OSRD reports, the reader is referred to OSRD 6630, the last report issued by Division 8. The report gives, for every report issued by the Division, the following information: the OSRD number and, for the very early reports, the former Division B serial number; the title; the name of the author or authors; the month and year of issue; the number of pages, illustrations, and tables; the pertinent Army and Navy project numbers; and an abstract. There is also a subject index.

Finally, attention should be called to two reports of general interest: OSRD 5401, which is an introduction to both the theoretical and the practical aspects of explosives and explosions; and OSRD 2014, which is a compilation of data on the properties of explosives.

Chapter 1

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224. *The Separation of Nitroglycerine from Double-Base Powders, A Preliminary Literature Survey*, F. H. Westheimer, OSRD 4791, OEMsr-202, Service Project OD-01, Explosives Research Laboratory, Carnegie Institute of Technology, Mar. 9, 1945. Div. 8-604.2-M3

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227. *Spontaneous Ignitors for Gasoline-Fuming Nitric Acid Mixtures*, Eugene E. Ayres, OSRD 1000, OEMsr-322, Service Project NA-103, Final Report 421, to Sept. 30, 1942, Gulf Research and Development Company, Nov. 4, 1942. Div. 8-702-M2

228. *New and Improved Syntheses of Miscellaneous Organic Compounds*, Philip E. Wilcox, OSRD 5974, OEMsr-881, Service Projects NO-274 and OD-158, CIT, Nov. 27, 1945. Div. 8-602.1-M4

229. *The 32° Transition of Ammonium Nitrate*, J. F. Kincaid and R. C. C. St. George, OSRD 1577, OEMsr-202, Service Projects OD-05 and OD-14, ERL, Carnegie Institute of Technology, July 7, 1943. Div. 8-110.3-M3

Chapter 7

1. *Tracer Research at the Explosive Research Laboratory*, Walter Kauzmann, OSRD 3283, OEMsr-202, Service Projects NO-151 and OD-159, ERL, Carnegie Institute of Technology, Feb. 14, 1944. Div. 8-701-M2

2. *Review of Igniter and Tracer Compositions*, OSRD 3498, OEMsr-1226, Service Projects OD-159 and NO-151, Report to Mar. 15, 1944, Metal and Thermit Corporation, Apr. 21, 1944. Div. 8-701-M3

3. *Tracer and Igniter Compositions*, OSRD 6581, OEMsr-1226, Service Projects NO-151 and OD-159, Metal and Thermit Corporation, Jan. 15, 1946. Div. 8-700-M1

4. *Polarographic Analysis of Primers*, James J. Lingane, OSRD 4881, OEMsr-1028, Service Project OD-118, Harvard University, Mar. 30, 1945. Div. 8-703-M2

5. *The Microscopical Examination of Primer Compositions*, Alfred T. Blomquist, OSRD 3757, OEMsr-193, Service Project OD-109, Cornell University, Aug. 1, 1944. Div. 8-703-M1

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[redacted]

Contract Number	*Contractor*	*Subject*
NDCrc-4	University of Chicago Chicago, Ill.	Kinetics of nitration
NDCrc-5	Harvard University Cambridge, Mass.	Synthesis of aliphatic-aromatic nitro-compounds
NDCrc-7	Northwestern University Evanston, Ill.	Synthesis of Tetranitromethane
NDCrc-8	Pennsylvania State College State College, Pa.	Synthesis of RDX
NDCrc-12	Massachusetts Institute of Technology Cambridge, Mass.	Nitration of naphthalene
NDCrc-19	Iowa State College Ames, Iowa	Nitration of furans
NDCrc-21	University of Michigan Ann Arbor, Mich.	Synthesis of explosives from ethylenediamine
NDCrc-22	Polytechnic Institute of Brooklyn Brooklyn, N. Y.	Synthesis of aminoguanidine sulfate
NDCrc-23	Cornell University Ithaca, N. Y.	Synthesis of cyclic nitro compounds
NDCrc-24	Columbia University New York, N. Y.	Synthesis of explosives from amino alcohols
NDCrc-27	Massachusetts Institute of Technology Cambridge, Mass.	Nitration of wood pulp
NDCrc-30	Harvard University Cambridge, Mass.	Theory of detonations
NDCrc-35	Purdue University Lafayette, Ind.	Synthesis of nitroparaffins
NDCrc-43	Ohio State University Columbus, Ohio	Synthesis of explosive intermediates obtained by formaldehyde condensations
NDCrc-46	Harvard University Cambridge, Mass.	Measurement of heats of combustion of explosives
NDCrc-66	Pennsylvania State College State College, Pa.	Synthesis of RDX
NDCrc-87	University of Michigan Ann Arbor, Mich.	Synthesis of RDX
NDCrc-147	National Academy of Sciences Washington, D. C.	Phase rule diagrams of explosives
NDCrc-153	Massachusetts Institute of Technology Cambridge, Mass.	Conversion of nitrocellulose to smokeless powder
NDCrc-162	Columbia University New York, N. Y.	Synthesis of explosives from amino alcohols
NDCrc-168	Harvard University Cambridge, Mass.	Study of shock waves
OEMsr-11	Carnegie Institute of Technology Pittsburgh, Pa.	Explosives Research Laboratory
OEMsr-121	Cornell University Ithaca, N. Y.	Study of shock waves
OEMsr-137	Columbia University New York, N. Y.	Synthesis of explosives from amino alcohols
OEMsr-147	National Academy of Sciences Washington, D. C.	Separation of nitrotoluenes
OEMsr-156	National Academy of Sciences Washington, D. C.	Phase rule diagrams of explosives
OEMsr-163	Ohio State Research Foundation Columbus, Ohio	Eutectic diagrams of explosives
OEMsr-181	Western Cartridge Co. East Alton, Ill.	RDX pilot plant
OEMsr-193	Cornell University Ithaca, N. Y.	Synthesis of RDX, DINA, and other nitramines and the crystallographic identification of explosives
OEMsr-194	Monsanto Chemical Company Dayton, Ohio	Plastic binders for moulded composite propellants

Contract Number	*Contractor*	*Subject*
OEMsr-202	Carnegie Institute of Technology Pittsburgh, Pa.	Explosives Research Laboratory
OEMsr-210	University of Wisconsin Madison, Wis.	Gelatinization of nitrocellulose
OEMsr-218	Institute of Advanced Study Princeton, N. J.	Study of shock waves
OEMsr-220	E. I. du Pont de Nemours & Co. Wilmington, Del.	RDX pilot plant
OEMsr-224	Columbia University New York, N. Y.	Synthesis of explosive intermediates obtained by formaldehyde condensations
OEMsr-228	Cornell University Ithaca, N. Y.	Apparatus for determination of particle size
OEMsr-229	Cornell University Ithaca, N. Y.	Gelatinization of nitrocellulose
OEMsr-239	Pennsylvania State College State College, Pa.	Supply contract
OEMsr-243	Pennsylvania State College State College, Pa.	Synthesis of RDX
OEMsr-244	Pennsylvania State College State College, Pa.	Compilation of data on explosives
OEMsr-245	University of Michigan Ann Arbor, Mich.	Synthesis of RDX and picric acid
OEMsr-273	George Washington Univ. Washington, D. C.	Rocket propellants
OEMsr-305	Columbia University New York, N. Y.	Kinetics of nitration
OEMsr-322	Gulf Research & Development Company Pittsburgh, Pa.	Igniters for gasoline-nitric acid mixtures
OEMsr-334	Harvard University Cambridge, Mass.	Studies of detonations
OEMsr-342	Harvard University Cambridge, Mass.	Mechanisms of formation of RDX
OEMsr-351	Gulf Research & Development Company Pittsburgh, Pa.	Phlegmatization of RDX
OEMsr-373	E. I. du Pont de Nemours & Company Wilmington, Del.	Ethyleneurea pilot plant
OEMsr-393	Tennessee Eastman Corp. Kingsport, Tenn.	RDX pilot plant
OEMsr-397	Tennessee Eastman Corp. Kingsport, Tenn.	Incorporation of RDX with TNT
OEMsr-569*	Woods Hole Oceanographic Institution Woods Hole, Mass.	Underwater explosions
OEMsr-596*	Stanolind Oil & Gas Co. Tulsa, Okla.	Gauges for measurement of shock waves
OEMsr-616	Ohio State University Columbus, Ohio	X-ray studies of RDX
OEMsr-639	Monsanto Chemical Company Dayton, Ohio	Pilot plant for moulded composite propellants
OEMsr-640	E. I. du Pont de Nemours & Company Wilmington, Del.	Pilot plant for production of ethyleneurea from glycol
OEMsr-643	Rohm & Haas Company Philadelphia, Pa.	Synthesis of polymers of nitro compounds
OEMsr-646	University of Pennsylvania Philadelphia, Pa.	Synthesis of RDX, picric acid, and DINA
OEMsr-669	University of Notre Dame Notre Dame, Ind.	Addition of nitrogen oxides to ethylene
OEMsr-701	Indiana University Bloomington, Ind.	Synthesis of DINA and other nitramines
OEMsr-719	Hercules Powder Company Wilmington, Del.	Sensitivity of explosives
OEMsr-741	Queens College Flushing, N. Y.	Compilation of data on explosives

*Transferred to Division 2.

Contract Number	*Contractor*	*Subject*
OEMsr-751	Cornell University Ithaca, N. Y.	Underwater explosions
OEMsr-754	University of Pittsburgh Pittsburgh, Pa.	Measurements of heats of combustion of explosives
OEMsr-763	E. I. du Pont de Nemours & Company Wilmington, Del.	Preparation of special gun propellants
OEMsr-764	E. I. du Pont de Nemours & Company Wilmington, Del.	Study of shaped charge weapons
OEMsr-765	E. I. du Pont de Nemours & Company Wilmington, Del.	Haleite pilot plants
OEMsr-773	Johns Hopkins University Baltimore, Md.	Theory of shock waves
OEMsr-790	Vanderbilt University Nashville, Tenn.	Synthesis of nitramines
OEMsr-800	Standard Oil Development Company New York, N. Y.	Oils for desensitization of RDX
OEMsr-828	E. I. du Pont de Nemours & Company Wilmington, Del.	Explosive streamer
OEMsr-836	Eastman Kodak Company Rochester, N. Y.	New sources of wood cellulose for nitration
OEMsr-859	Hercules Powder Company Wilmington, Del.	Explosive streamer
OEMsr-875	University of Chicago Chicago, Ill.	Kinetics of nitration
OEMsr-881	California Institute of Technology Pasadena, Calif.	Chromatographic analysis of propellants
OEMsr-944*	New York University New York, N. Y.	Theory of shock waves
OEMsr-957	Princeton University Princeton, N. J.	Theory of detonations
OEMsr-959	Gulf Research and Development Company Pittsburgh, Pa.	Shaped charge weapons
OEMsr-962	University of Pennsylvania Philadelphia, Pa.	Health hazards in RDX manufacture
OEMsr-976	University of North Carolina Chapel Hill, N. C.	Theory of shock waves
OEMsr-1028	Harvard University Cambridge, Mass.	Polarographic analysis of explosives
OEMsr-1040	University of Wisconsin Madison, Wis.	Polarographic analysis of explosives
OEMsr-1118	E. I. du Pont de Nemours & Company Wilmington, Del.	Design of an ethyleneurea plant
OEMsr-1126	Phillips Petroleum Company Bartlesville, Okla.	Design of a cyclopentanone plant
OEMsr-1145	Gulf Research & Development Company Pittsburgh, Pa.	Ignition system for rocket propellants
OEMsr-1152	Ohio State University Research Foundation Columbus, Ohio	Decomposition products of nitrocellulose
OEMsr-1216	American Aircraft Association Dayton, Ohio	Jet propulsion motors
OEMsr-1226	Metal & Thermit Corporation Rahway, N. J.	Igniters and tracers
OEMsr-1332	E. I. du Pont de Nemours & Company Wilmington, Del.	DINA pilot plant
OEMsr-1355	E. I. du Pont de Nemours & Company Wilmington, Del.	Pilot plant for special gun propellants
OEMsr-1462	Western Electric Company New York, N. Y.	Development of an acoustical method for detection of flaws in powder grains
OEMsr-1467	E. I. du Pont de Nemours & Company Wilmington, Del.	Development of inert simulants of explosives

* Transferred to Applied Mathematics Panel.

SERVICE PROJECT NUMBERS

The projects listed below were transmitted to the Executive Secretary, National Defense Research Committee, NDRC, from the War or Navy Department through either the War Department Liaison Officer for NDRC or the Office of Research and Inventions (formerly the Coordinator of Research and Development), Navy Department.

Service Project Number	*Title*
AC-75	The Development and Testing of Solid Propellants and Motors for Jet Propulsion Devices Requiring Large Propellant Grains
AN-1	Shaped Charges
CE-30	Munroe Effect of Explosives. (Proj. cancelled)
CE-32	Project on the Development of a Hose Filled with Explosive for Mine Field Clearance
	Extended to include: "Indicator" Mine (a) Fabric Snake
NA-103	Self-Igniting Chemical for Jet Propulsion
NA-197	Development of Jet Assisted Take-Off Unit for Carrier Based Aircraft
NO-B10	Development of New Explosives
NO-B38	Mixing Methods for BWX and RDX
NO-B39	Smokeless Powder, Wood Cellulose for Nitration, Conversion of Nitro-Cellulose into Smokeless Powder
NO-B40	Phlegmatization of TNT for Loading AP Shells
NO-99	Jet Propulsion
NO-110	Controlled Fragmentation
	Extended to include: Fragmentation of Light Case Bombs or Rocket Ammunition
NO-116	Scatter Bomb for Submarine Attack by Heavier-than-Aircraft
NO-117	Process which will be Useful in Alleviating Phenol Shortage
NO-133	Coned Charges in: Antisubmarine Scatter-Bombs and Torpedo Warheads
NO-135	Flashless Powder Suitable for Use in 6″ and 8″ Navy Guns
	Extended to include: Albanite Powder
	Albanite Powder Granulation Samples
	Development of Certain Powder Samples of Albanite Cordite-N
NO-138	Determination of Proper Booster System for Large Explosive Charges. (Transferred to Division 2)
NO-151	Method of Loading Tracers
NO-167	Retardation of Projectile Fragments
NO-199	Study of Storage on TNT
NO-201	Effect of Heat on Confined Explosives
NO-211	Technique of Handling Composition A
NO-212	Development of Uniform Primacord
NO-213	Development of Propellant Powders for High Pressures and Densities of Loading
NO-223	Investigation of Explosives for Use in Underwater Munitions. (Transferred to Division 2)
NO-224	Theoretical Investigation of Explosion Phenomena. (Transferred to Division 2)
NO-231	Investigation of Physical and Chemical Properties of Aluminized Explosives
NO-232	Desensitization of Service Munitions
NO-237	Determination of Depth of Underwater Explosions from Surface Observations. (Transferred to Division 2)
NO-274	Stabilizers, Surveillance Methods, and Stability of Rocket Propellants
NO-290	Preparation and Testing of Military Explosives
NO-291	Optical Phenomena of Explosions
NS-125	Design of an Explosive Streamer
NS-267	NDRC Assistance in Underwater Explosion Measurements on Submarine Models. (Transferred to Division 2)
NS-309	3-inch Solid Slow-Burning Propellants. (Transferred to Division 3)
OD-01	Testing of Chemicals as Military High Explosives. Evaluation of Two (2) Types of Composition B/tetryl Explosives
OD-02	Basic Study of Detonations
OD-04	Fundamental Research in High Explosives Such as Phlegmatization, Etc.
OD-05	Special Propellants
OD-1	Study of Nitration of Furan and Derivatives
OD-2	Preparation of Nitroparaffins and of Certain Derivatives Thereof

Service Project Number	*Title*
OD-3	Preparation of Amino Guanidine Sulfate and of Tetracene
OD-4	Formaldehyde Condensations with Aldehydes and Ketones and Nitration of Products
OD-5	A. Preparation of Nitrocyclohexane Derivatives
	B. Methods of Preparation of T.N.B., and
	C. Ethyleneimine Derivatives for Explosives and Toxic Substances
OD-6	Preparation of Explosives from Ethylene Urea and Related Substances: Preparation of T.N.B. Amended 12-29-42 to read: "Preparation of Explosives from Substances Relating to Ethyleneurea and Compounds Analogous Thereto"
OD-7	Preparation of Explosives from Mono-, Di-, and Triethanolamines
OD-8	Preparation of Mixed Aliphatic-Aromatic Nitro Compounds and Nitrate Esters
OD-9	Kinetics of Nitration of Toluene, Xylene, Benzene, and Ethylbenzene
OD-10	A. Use of Acids Other Than Sulfuric in Nitration Mixtures
	B. Preparation of T.N.B.: *Meta*-Xylene from Crude Xylene
OD-11	A. Preparation of Tetranitromethane
	B. Nitroform and Condensation Products
	C. Nitration of Ethylene and Acetylene
OD-12	Nitration of Hexamethylene Tetramine and Analogous Compounds
	Extended to include: Chromatographic Determination of the HMX Content of RDX
OD-13	Nitration of Naphthalene and Naphthol
OD-14	Special Fuels for Jet Propulsion
OD-15	Preparation of Special Compounds
OD-21	Use of Oxyhydrogen as an Explosive
OD-22	Research on Possible Source of Nitrocellulose
OD-23	Nitration and its Relationship to Detonating or Tonal Wave
OD-29	Preparation of Glucose Perchlorate and the Production of Glucose from Lignin Wastes
OD-31	Improvement and Visibility of High Explosive Shell Bursts—Day and Night
OD-44	Accelerants for the Gelatinization of Nitrocellulose
OD-58	The Stability of PETN and its Mixture with TNT
OD-68	Development of Raw Materials for the Manufacture of EDNA, Ethylenedinitramine
OD-77	Suitability of N.I.P. as Substitute for Charcoal and Methods of Manufacturing
OD-103	Development of a Composition C (RDX-C) Explosive having a Satisfactory Plasticity at Low Temperatures, Without Sacrifice of Sensitivity and Other Performance Characteristics
OD-109	The Microscopic Method for the Qualitative Detection of Explosive Components
OD-118	The Application of Polarographic Analysis to Military High Explosives
OD-126	The Determination of the Structure of the Organic Intermediate Molecules Occurring in the Burning of Propellant Powders
OD-131	Mine Case M3A1. (Transferred to Division 2)
OD-152	Data on the Retardation of Fragments in the Air and Their Perforation of Steel Plate
OD-158	Studies of Characteristics of New Double-Base Propellant Compositions
OD-159	Development of Igniter-Tracer Units
OD-188	High Impulse Light Weight Rocket Motors (Project declined April 13, 1945)
OD-197	Development and Application of Cast Double Base Propellants
OD-198	Development and Application of Composite Propellants
OD-200	BBP Charge for Heavy-head M6A4 Type Rocket
OD-201	Research on Elements of Rocket Motors with High Impulse Ratio
SC-41	Microwave Tube Destruction
SOS-10	Investigation of Nitroso Guanidine and Other Compounds as Gas Generators

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